SYNTHESIS AND PROPERTIES OF π-STACKED PHENYLENE ETHYNYLENE OLIGOMERS WITH A 1,8-SUBSTITUTED NAPHTHALENE BRIDGING SCAFFOLD

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SYNTHESIS AND PROPERTIES OF

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To Mom, Dad, and Rebecca

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LIST OF SYMBOLS AND ABBREVIATIONS

π	Pi
δ	Chemical shift (specific to NMR)
NMR	Nuclear Magnetic Resonance
λ	Wavelength
ε	Molar Absorptivity
J	Coupling constant
ppm	Parts per million
Hz	Hertz
d	Doublet
dd	Doublet of Doublets
t	Triplet
s	Singlet
m	Multiplet
PE	Phenylene ethynylene
PPE	Poly(phenylene ethynylene)
THF	Tetrahydrofuran
Th	Thiophene
IR	Infrared (Spectroscopy)
CV	Cyclic Voltammetry
DPV	Differential Pulse Voltammetry
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital

EI	Electron Ionization
HRMS	High Resolution Mass Spectrum
XRCS	X-Ray Crystal Structure
$E_{1/2}$	Half-wave oxidation potential
DMF	N,N-Dimethylformamide

SUMMARY

The field of molecular electronics includes the study of conjugated oligomers and polymers that have significant potential for use in devices such as light emitting diodes (LEDS), field effect transistors (FETS), and photovoltaic solar cells. These materials may replace inorganic semiconductors in these devices, Achieving better device performance through lowering the band-gap and achieving higher field effect mobilities will benefit from a greater fundamental understanding of charge transfer through the aromatic subunits. π-stacking of segments of conjugated polymers has been identified as a key feature that influences the charge transfer through semiconducting organic materials. Optimizing the molecular architecture of conjugated polymers has the potential to provide materials with better charge mobility. While devices might benefit from materials that take advantage of π-stacking, access to π-stacked structures presents a synthetic challenge. 1,8-Disubstituted naphthalenes may serve as simple covalent bridging scaffolds which might hold conjugated oligomers in a π-stacked arrangement. The research described in this thesis focuses on the synthesis of well-defined phenylene ethynylene oligomers coupled to naphthalene to serve as experimental models of closely π-stacked aromatic units in conjugated polymers. The π-stacked molecules reported in this dissertation are characterized by NMR, IR, and mass spectrometry. The effects of π-stacking on the structure and behavior of conjugated oligomers are determined by X-ray crystallography, spectroscopy, and electrochemistry.

CHAPTER 1

INTRODUCTION TO ELECTRONIC PROPERTIES OF CONJUGATED OLIGOMERS AND POLYMERS

1.1. Molecular Electronics

The role of conjugated polymers in the field of molecular electronics is beginning to drive research that has potential economic benefit to microelectronics with the preparation of new materials for electronic circuitry,[1-2] transistors,[3-8] sensors,[9] photovoltaic solar cells,[10] and light-emitting diodes (LEDs).[11-12] This initiative began with the discovery of polyacetylene which was recognized with the award of the Nobel prize in 2000 to Heeger, MacDiarmid, and Shirakawa.[13] New classes of semiconducting organic materials include conjugated oligomers and polymers in which every other bond is a double or triple bond, which may include aromatic units. Polymers that have received extensive attention include poly(2-methoxy-5-ethylhexyloxy-phenylene vinylene) (MEH-PPV),[14] poly(3-hexylthiophene) (P3HT),[15] poly(diethylhexylfluorene) (DEH-PF),[16] poly(*para*-phenylene) (PPP),[17] and poly(1,4-phenylene ethynylene) (PPE),[18] Figure 1.1. These may find application in electronic devices due to their potential ease in processability, tunability of properties by molecular design, low density, and mechanical flexibility.

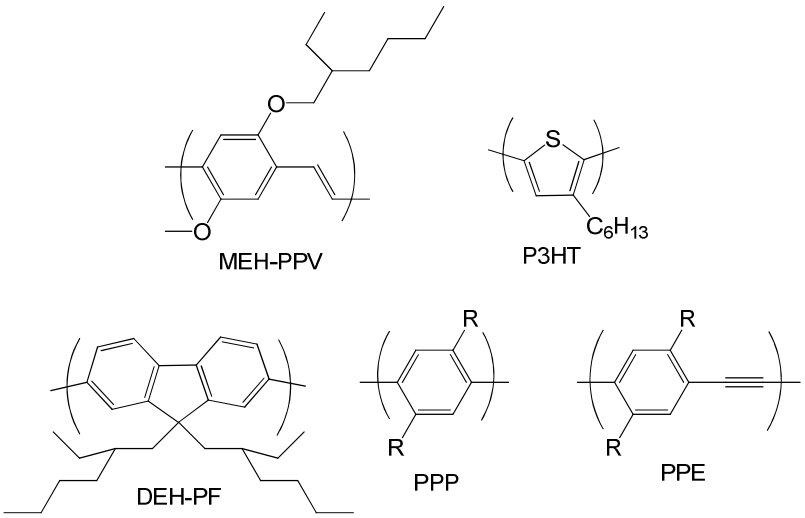

Figure 1.1. Repeat units of some of the most studied conjugated polymers. See text for corresponding references.

1.2. Charge Transfer in π-Conjugated Materials

Electrons that reside in p-orbitals undergo π-bonding from orbital overlap. The electrons that are in the ground-state occupy the bonding orbitals where the electrons that are in the HOMO (highest occupied molecular orbital) can undergo excitation through a dipole-allowed transition to the LUMO (lowest unoccupied molecular orbital), which is an anti-bonding orbital. The Frost mnemonic in Figure 1.2 shows that for a simple π-bonded structure such as ethylene in the ground state, there is a π-bonding orbital occupied by two electrons and a vacant anti-bonding π-orbital but as there is a progression to a longer-chain polyene such as trans-polyacetylene, a band regime emerges that mimics the properties of a semiconductor.[19] Electrons in the ground state comprise the valence band, but these can be thermally excited to occupy the conduction band.

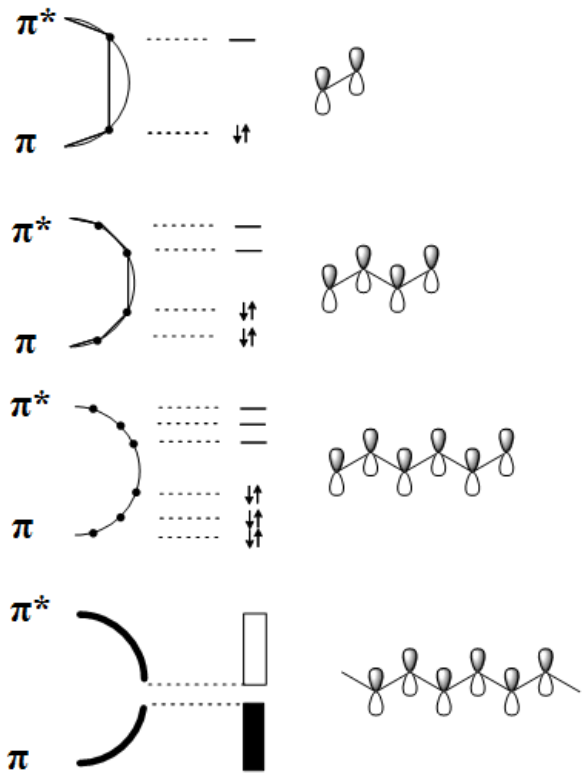

Figure 1.2. Frost mnemonic for polyene π-orbitals depicting evolution of the valence band and the conduction band.[19]

Doping an organic semiconductor is a process where an oxidant or reductant is added to improve the conductivity of the material. In Shirakawa's investigation of electrically-conducting films of polyacetylene, it was necessary to treat the films with molecular bromine in order to achieve conductivity.[13] Understanding how dopants improve charge transport, and exploring charge transport in two dimensions, may offer the potential to develop materials with conductivity close to that of a metal.

Oxidative (p-type) doping corresponds to removal of π-electrons from the valence band of a conjugated polymer, and leads to the formation of positive charge carriers. These are often referred to as polarons, which are equivalent to cations (+1).[20] Additional

oxidation will produce a delocalized dication. Polarons and bipolarons are thought to be the primary form of charges that migrate through a p-doped polymer film in response to an applied potential (Figure 1.3)

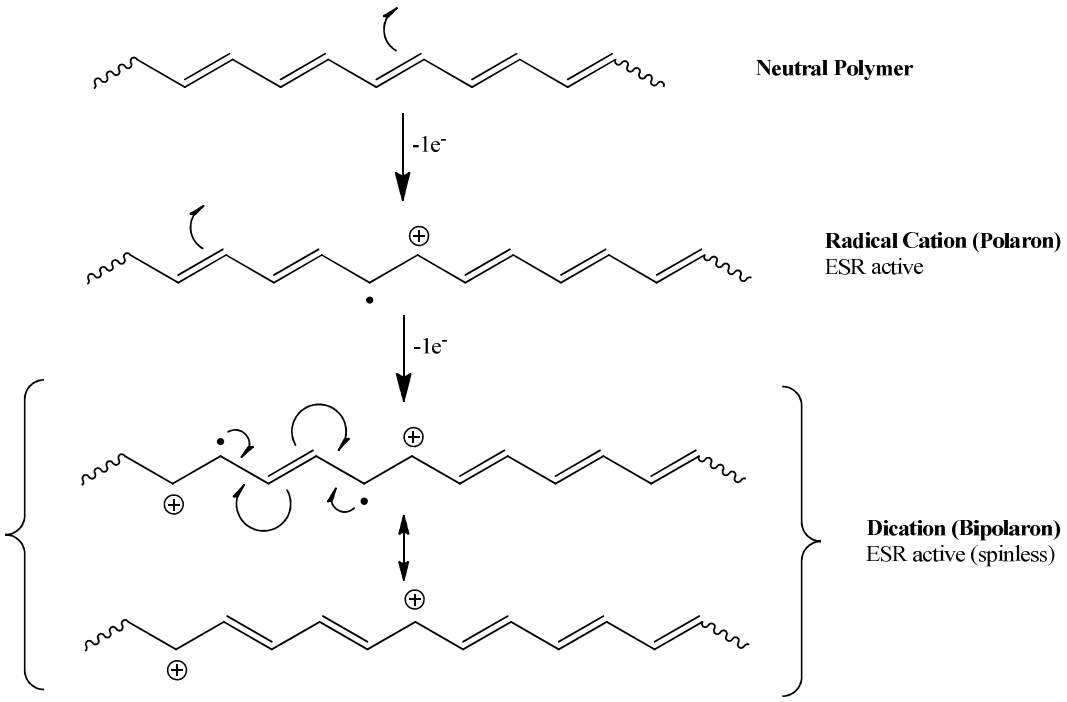

Figure 1.3. Example of the different charge carriers, polarons and bipolarons for a conjugated polymer like polyacetylene.

1.3. Charge Transfer and the Importance of π-Stacking

In the late 1980s and through the 1990s, Diaz and Tour,[21] Miller[22-29] and Bäuerle[30-31] performed a series of studies on α, α-coupled thiophene oligomers (n=2-8) to explore the electronic and spectroscopic properties of polarons and bipolarons. The conjugation length was sufficient to form cations and dications upon oxidation of the oligomers. In one of Miller's reports, the oligomers were electrochemically oxidized and the UV-vis-near-IR spectra measured in a temperature controlled spectrometer cell where Figure 1.4 provides a summary of the results collected.[25] The absorption spectrum of the

molecular species of the trimer was identified as a single peak at 360 nm. Upon one-electron oxidation of a thiophene trimer (Th_3), spectra taken at room temperature showed new absorption peaks at a longer wavelength at 572 and 880 nm which was assigned to the delocalized cationic form (Th_3^+). Upon cooling or adding of a poor solvent, peaks at 466, 708, and 868 nm appeared. These were assigned to a species referred to as a radical cation π-dimer $(Th_3^+)_2$ as depicted in Figure 1.5. A separate experiment where the oligomers underwent a two-electron oxidation at -10ºC gave an absorption peak at 570 nm was identified as the dication (Th_3^{+2}).

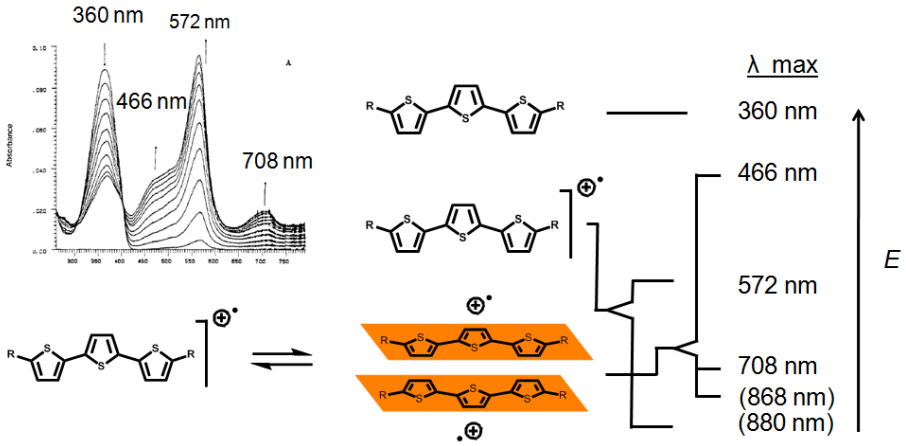

Figure 1.4. Summary of the experimental results from the spectroelectrochemical absorption measurements and corresponding charge species assignments or a thiophene trimer (Th_3), thiophene trimer cation (Th_3^+), and thiophene trimer radical cation dimer $(Th_3^+)_2$ reported by Miller.[25]

A proposed molecular orbital diagram in Figure 1.5 by Miller,[25] Bauerle,[30] Tour,[21] and Reynolds[32] sets out to explain the electronic structure of the π-dimer species. They suggest that two overlapping π-orbitals of radical cations undergo an exchange of π-electrons to form new hybridized orbitals. This shows that singly occupied orbitals of the

radical cations can interact to form a spin-paired orbital that is lower in energy with new dipole allowed transitions that are lower than that of the independent cation. Therefore, this identifies that π-stacking in a material can be constructive to the valence band and destructive to the conduction band thereby lowering the band gap energy of a semiconductor. Based on Miller's observations of radical cation π-dimers, the interaction of these ions (under certain conditions, i.e. low temperature, poor solvent, or high concentration) is an energetically favorable process which overcomes Coulombic repulsion.

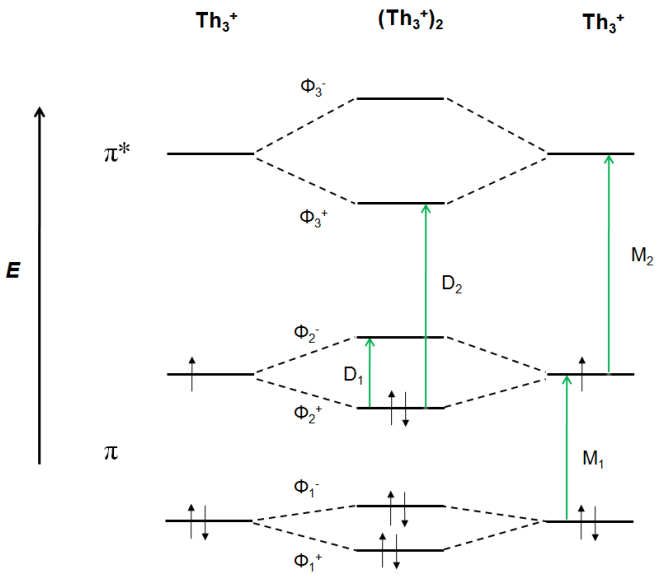

Figure 1.5. Proposed MO diagram for a thiophene trimer (Th_3) radical cation π-dimer species and plausible dipole allowed transitions that account for the corresponding spectral absorptions.[21,30]

While π-dimers have been proposed as an alternative to bipolarons as charge carriers in conjugated polymers, several other scenarios are possible upon bringing radical cations into close proximity. A pair of radical cations can undergo

disproportionation to produce a neutral species and a dication. They may also combine to form a sigma bond, leaving two cations (i.e. σ-dimerization). In certain cases, σ-dimers have been suggested as possible charge carriers.[33] Figure 1.6 summarizes the charge interactions between radical ions.

DISISOPROPORTIONATION

$$M^{+\cdot} + M^{+\cdot} \rightarrow M^{2+} + M^{0}$$

BIS(RADICAL CATION) COMBINATION

$$M^{2(+\cdot)} \rightarrow M^{2+}$$

σ-DIMERIZATION

$$M^{+\cdot} + M^{+\cdot} \rightarrow M^{+}—M^{+}$$

π-DIMERIZATION

$$M^{+\cdot}—M^{+\cdot} \rightarrow (M—M)^{2+/0}$$

Figure 1.6. Possible charge interaction scenarios associated with radical ions.

Many fundamental questions about charge transfer through π-stacking remain. While it is common to observe π-stacking interactions between conjugated chains with intermolecular distance under 5Å, it is still unclear as to how the structure of the chain and orientation might produce an optimal electronic interaction amongst conjugated chains in a material. Two planarized segments of conjugated polymers with like charges in an electrically conducting film would closely resemble the π-dimer species identified by Miller. One method of probing π-π interactions is with models where two conjugated oligomer segments are joined by a covalent bridge.

1.4. Covalent Linkage of Conjugated Chains to Hold in π-Stacked Orientations

Several bridging scaffolds that have been identified to provide access to covalently-bound conjugated oligomers held in a π-stacked orientation. [2.2]Paracyclophane is a π-stacking unit of two benzenes with ethylene bridges in the 1 and 4 positions of the benzene to induce co-facial overlap of the rings. Bazan,[34-36] Chujo,[37-39] and Collard[40-41] have reported on the use of para[2.2]cyclophane as a bridging unit in conjugated oligomers and polymers. The conjugated units interact through the cyclophane π-stacked unit. Large Stokes shifts can be attributed to excitation of a single conjugated unit followed by energy transfer in the excited state to a lower energy "phane state" which is the chromophore species that then emits light.

Reports from the early 1960s on π-stacking interactions used 1,8-naphthalenes[42-43] and anthracenes[44] as bridging scaffolds. The crystal structure of 1,8-diphenylnaphthalene reveals that the phenyl subunits are held co-facially at a distance of 2.4 Å. The 1,8-naphthyl unit is one of the simplest designs for a scaffold that has two bonds that are parallel to one another. The ease in design made it attractive to append more extended conjugated chains onto this scaffold to explore the effect of stacking on the electronic structure of π-systems.

1.5. Scope of Work

Our approach to exploring π-stacks of aromatic subunits of conjugated polymers involves the coupling of phenylene ethynylene (PE) oligomers onto a 1,8-diiodonaphthalene scaffold. These oligomers are models for subunits of conjugated polymers that replicate the intermolecular interactions between chains in films. The

stacked oligomers can be characterized in solution since the covalent bridge ensures that π-stacking is retained. The 1,4-phenylene ethynylene (PE) subunit is linear, and poly (PEs) (PPEs) and PE oligomers generally have a low degree of curvature (i.e., they are rigid rods). Phenylene ethynylenes are conveniently prepared by Sonogashira coupling of synthetically accessible aryl diiodides and diethynylarenes. We used step-by-step synthetic protocols to prepare oligomers with two different substitution patterns (Figure 1.7): (1) oligomers with two alkoxy side chains on each phenylene subunit (Chapter 2 and 3), and (2) those with a single alkoxy group at the terminus of the oligomer (Chapter 4).

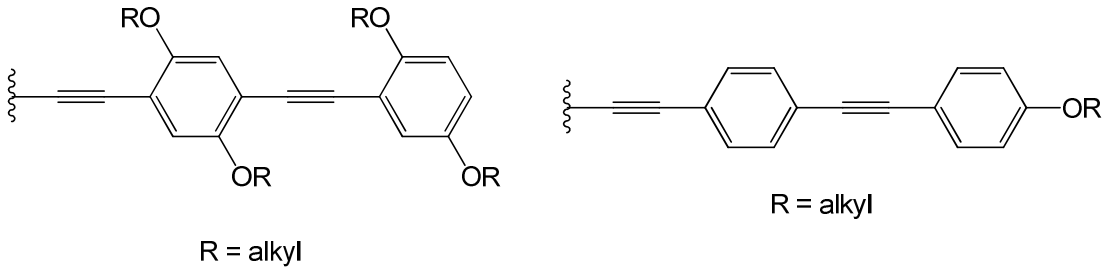

Figure 1.7. Two types of 1,4-phenylene ethynylene oligomers used in this study: oligomers with two alkoxy side chains on each phenylene subunit (left), and with a single alkoxy group at the terminus (right).

The 1,8-naphthalene scaffold has been shown by House to be well-suited for building covalently-bound π-stacked structures. Accordingly, we set out to substitute our oligomers onto the naphthalene core to explore the influence of π-stacking on the electronic properties (Figure 1.8).

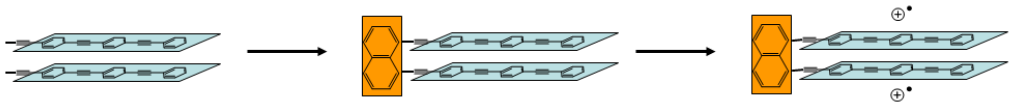

Figure 1.8. Two phenylene ethynylene oligomers bound to a naphthalene scaffold with aromatic units in a co-facial orientation to form a π-stack. The stacked radical cation resembles a radical cation π-dimer.

We have also extended π-stacking to beyond two-tiered systems. Nakayama[45-47] and Iyoda[48-49] have developed oligo(thiophene)s bound by 1,8-naphthalenes to make three- and four-tiered stacks. In Chapter 3 we report a modification to this approach for an oligo(PE) triad. In this synthesis, naphthalene was substituted with just one equivalent of oligomer which served as the external "arms." These arms were then coupled to a common di-alkyne "core," Figure 1.9, to offer a simple convergent approach to afford a three-tiered oligomer.

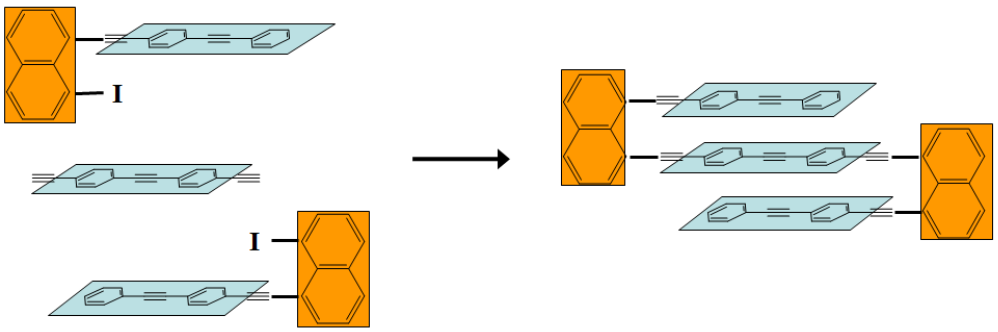

Figure 1.9. Approach for making a three-tiered PE oligomer.

Macrocycles such as those reported by Iyoda[48-49] are of interest in future studies of π-stacked structures. The 1,8-substituted naphthalene may be used to hold conjugated oligomers in a π-stacked macrocycle. The ring-closed structure will closely resemble that of paracyclophane having a restricting geometry that will force oligomers into eclipsing π-stacks. In Chapter 5, we discuss a synthetic route to macrocycles using dialkoxy PEs to make π-stacked oligomers, a depiction of this approach is shown in Figure 1.10.

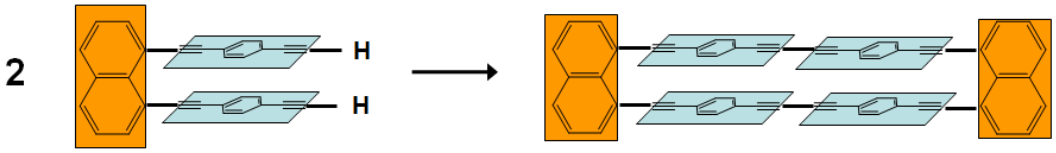

Figure 1.10. Illustration of an approach for making a macrocycle.

Several characterization methods can be used to measure the interaction of these π-stacked systems. Crystallography data will give insights into the structure of stacked aromatic units. Photophysical measurements can identify the absorption and emission properties associated with two closely-joined conjugated oligomers. Electrochemical measurements can identify trends in oxidation potential as a function of electronic interaction amongst the conjugated oligomers.

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CHAPTER 2

SYNTHESIS AND CHARACTERIZATION, OF BIS (OLIGO (2,5-DIPROPYLOXY)-1,4-PHENYLENE ETHYNYL)-1,8-NAPHTHALENES

2.1. Introduction

The discovery of polyacetylene[1] has driven research on a broad range of conjugated polymers for application in devices such as organic light-emitting diodes (OLEDs),[2] field effect transistors (FETs),[3-5] and photovoltaic solar cells.[6] The conjugated polymers may offer an advantage over conventional inorganic semiconductors as they are mechanically flexible, low cost, durable, and may offer better performance in selected applications. Attention has been focused on the development of new types of conjugated polymers with enhanced properties that are suitable for integration in devices.

Poly(1,4-phenylene ethynylene)s (PPE) are a class of conjugated polymers with potential use in OLEDs. They are resistant to oxidative degredation, exhibit good hole conduction, and possess high electroluminescent efficiency.[7-12] These polymers are often adorned with electron-donating alkoxy side chains that raise the level of the HOMO so as to narrow the band-gap. In addition, the alkyl chains afford high solubility in organic solvents, which facilitates the preparation of uniform films by spin-coating, annealing, or spray/ink-jet printing for the fabrication of devices.[13] Whereas the double bond of poly(phenylene vinylene)s imparts a non-linear structure and to the presence of cis/trans isomers, the linear C-C triple-bond of PPEs contributes to a rigid linear structure.[8] The synthesis of PPEs is straightforward and capable of including different repeat units and

side chains. This can help to enable the development of polymers that have properties of supramolecular ordering for enhanced performance in electronic devices.[14]

Charge transport clearly involves interaction between neighboring chains, and one approach to develop polymers with good charge transport properties is to attain control over inter-chain interactions.[15-18] In electrically conducting films of conjugated polymers, planarized segments of chains that are co-facially overlapped thus having π-interactions can resemble the π-dimer species identified by Miller[18] when one charge is localized to each segment of the π-stacked chains. Identifying conditions that can take advantage of π-stacking interactions can lower the band-gap of the material and increase the field effect mobility.

Conjugated polymers and fused arenes which crystallized posses high field effect mobilities. For example, pentacene has a mobility of 0.5 $cm^2/(V \cdot s)$. Pentacene can have different crystalline polymorphs where it is believed there are a high degree of π-stacking interactions within these crystals.[19-21] The correlation between the crystal structure and high mobilities of conjugated materials identifies a need to develop a fundamental understanding of the nature of inter-chain interactions on the electronic structure and charge transport properties of the materials.

With the prospective application of PPEs in organic electronic devices, this study focuses on the synthesis of phenylene ethynylene oligomers as models to explore π-stacking interactions in conjugated polymers. The oligomers that we have prepared have the same repeat units as long polymeric PPE analogs.

There are many synthetic strategies to developing well-defined oligomers held in a stacked arrangment.[13-14,22-30] In studies of conjugated oligomers held π-stacked

structures, Collard,[31-32] Chujo,[33-36] and Bazan[37-39] have employed paracyclophane as a scaffold. The cyclophane unit brings the conjugated units into contact with one another in a defined manner. These authors have identified that π-stacking of these components contributes to a lowering of the redox potential compared to analogous unstacked oligomers, and the UV-vis absorbances are shifted to longer wavelength.

Reports from several authors use 1,8-substituted naphthalene as a "bridge" to hold arenes in π-stacked structures. House,[37-42] Siegel,[43-44] Roberts,[45-46] and Whiting[47] have all reported the synthesis of phenyl-substitued naphthalene derivatives. Nakayama[47-50] and Iyoda[51] have also used 1,8-substituted naphthalenes to prepare π-stacked thiophenes. In this study, we use 1,8-diiodonaphthalene to couple two phenylene ethynylene oligomers so the naphthalene serves as a bridging unit to hold the oligomers in a close proximity to one another. Short-alkyl propyloxy side chains are included in the design of our oligomers to afford solubility and structural analogy to dialkoxy PEs. Ultimately, we aim to explore the electronic effects of intermolecular interactions amongst segments of conjugated polymers with models of naphthalene-bridged conjugated oligomers. Characterization of our oligomers include X-ray crystallography, UV-vis/near IR absorption spectroscopy, fluorescence spectroscopy, and electrochemistry measurements.

2.2. Experimental

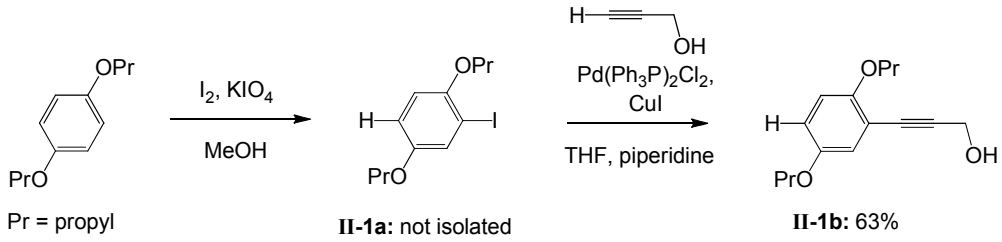
2.2.1. General Procedures

All reactions were conducted in distilled solvents in oven-dried and argon-charged glassware. All reagents were used as received from commercial suppliers without prior purification. Analytical thin layer chromatography (TLC) was performed on precoated aluminum-backed plates purchased from Sorbent Technologies (silica gel 60 F254; 0.25 mm thickness). Flash column chromatography was performed on silica gel 60 (230-400 mesh ASTM) from Sorbent Technologies. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer (300 MHz for ^{1}H, 100 MHz for ^{13}C). NMR spectra were measured in solutions of deuterated chloroform ($CDCl_3$) with tetramethylsilane as the internal standard. Chemical shifts are reported in parts per million (ppm). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; m, multiplet.

IR spectra were collected on a Nicolet 4700 FTIR with an ATR attachment from SmartOrbit Thermoelectronic Corp with samples as neat films. Mass spectra including high resolution were measured by EI on a Waters 70SE instrument or MALDI Micromass TofSpec2E instrument. Elemental analyses were obtained from Atlantic Microlabs in Norcross, Georgia. UV-vis/near-IR was recorded on a Perkin-Elmer Lamda 19 spectrometer. Fluorescence measurements were made on a Shimadzu RF-5301 PC in solutions in dichloromethane at ~10^{-6} M. X-ray Crystal structures were collected on a Bruker Apex-II CCD by Kenneth Hardcastle at Emory University X-ray facility.

2.2.2. Synthetic Procedures

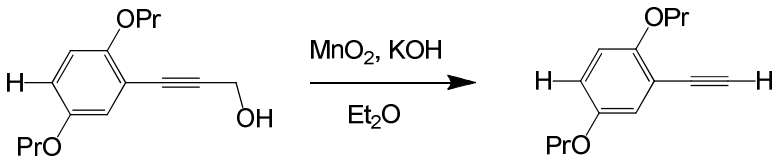
1,8-Diiodonapthalene,[41] 1,4-dipropyloxybenzene, and 1,4-diiodo-2,5-dipropoxybenzene[13] were prepared according to literature procedures.



1-(2,5-Dipropoxyphenyl)propyn-3-ol, II-1b. A solution of 1,4-dipropoxybenzene (10.0 g, 51.5 mmol), I_2 (6.54 g, 25.8 mmol), KIO_4 (5.93 g, 25.8 mmol), and conc. H_2SO_4 (1 mL) in MeOH (515 mL) was heated at reflux for 12 h. Saturated aqueous sodium sulfite (250 mL) was added and the mixture was extracted with Et_2O (250 mL). The organic extract was washed with saturated aqueous sodium sulfite (250 mL) and H_2O (250 mL). The solvent was removed under reduced pressure and the residue was recrystallized from methanol to give a 95:5 mixture of 1-iodo-2,5-dipropoxybenzene and 1,4-di-iodo-2,5-dipropoxybenzene which was used without further purification. *1-Iodo-2,5-dipropyloxybenzene,* **II-1a***:* ^{1}H NMR ($CDCl_3$): δ 0.99-1.11 (m, 6 H, CH_3), 1.70-1.89 (m, 4 H, CH_2), 1.71-1.89 (m, 4 H, CH_2), 3.84 (t, ^3J = 7 Hz, OCH_2), 3.90 (t, ^3J = 7 Hz, OCH_2), 6.72 (d, ^3J = 9 Hz, 1 H, Ar-6H), 6.84 (dd, ^4J = 3 Hz, ^3J = 9 Hz, 1 H, Ar-4H), 7.34 (d, ^4J = 3 Hz, 1 H, Ar-3H). MS (EI): m/z (%) 320.1 (75)[M+]. HRMS calculated for $C_{12}H_{17}O_2I$, 320.02733; found 320.02715, Δ = 0.6 ppm.

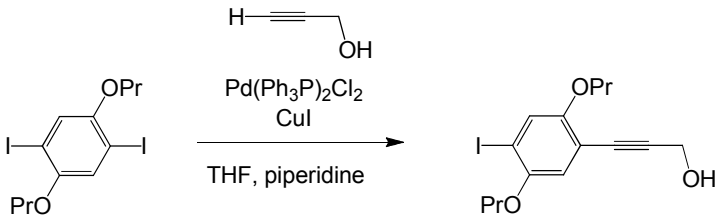
Propargyl alcohol (9.92 mL, 172 mmol), $Pd(Ph_3P)Cl_2$ (242 mg, 345 μmol), and CuI (131 mg, 690 μmol) in 510 mL of 1:1 THF and piperidine was added to a mixture of

the crude 1-iodo-2,5-dipropoxybenzene mixture under Ar. The mixture was stirred at room temperature for 12 h. Et_2O (200 mL) was added and the solution was washed with sat. aq. NH_4Cl (200 mL), and H_2O (200 mL). The solvent was removed under reduced pressure and the residue was extracted with hexane (200 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (25% v/v ethyl acetate:hexanes) to afford the title compound **II-1b** as an off-white crystalline solid (7.23 g, 63% yield for two steps). m.p. = 58-60 ºC. ^{1}H NMR ($CDCl_3$): δ 0.955 (t, ^3J = 8 Hz, 3 H, CH_3), 0.981 (t, ^3J = 8 Hz, 3 H, CH_3), 1.69-1.79 (m, 4 H, 2 CH_2), 2.95 (s, 1 H, -OH), 3.78 (t, ^3J = 7 Hz, 2 H, OCH_2), 3.88 (t, ^3J = 7 Hz, 2 H, OCH_2), 4.46 (s, 1 H, $C{\equiv}CCH_2$), 4.47 (s, 1 H, $C{\equiv}CCH_2$), 6.73 (d, ^3J = 12 Hz, 1H, Ar-6H) 6.77 (dd, ^4J = 3 Hz, ^3J = 8 Hz, 1H, Ar-5H), 6.89 (d, ^4J = 3 Hz, 1 H, Ar-3H). ^{13}CNMR ($CDCl_3$): δ 10.3 (CH_3), 22.4 (CH_2), 51.4 (CH_2OH), 70.0 (OCH_2), 71.1 (OCH_2), 81.6 (≡C-), 91.1 (Ar-C≡), 112.8 (Ar C-2), 113.9 (Ar C-6), 116.4 (Ar C-5), 118.6 (Ar C-3), 152.5 (Ar C-1), 153.7 (Ar C-4). IR (AT-IR, neat): 3378, 2963, 2934, 2875, 2227, 2154, 1604, 1497, 1467, 1414, 1387, 1265, 1225, 1183, 1142, 1023, 802, 752 cm^{-1}. MS (EI): m/z (%) 248.2 (100) [M+], 188.1 (35), 146 (77). HRMS calculated for $C_{15}H_{20}O_3$, 248.14272; found 248.14124, Δ = -5.9 ppm.



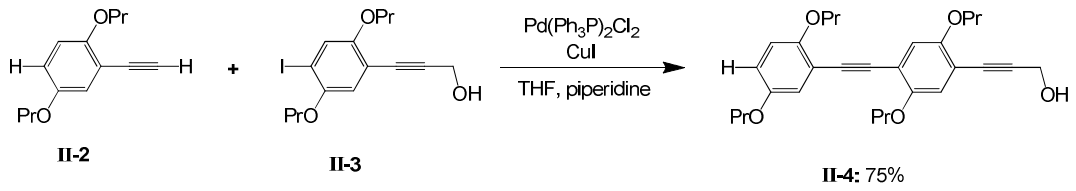
II-2: 88%

2-Ethynyl-1,4-dipropyloxybenzene, II-2. A mixture of MnO_2 (19.7 g, 227 mmol) and crushed KOH (12.5 g, 227 mmol) was added in four separate portions 1 hr apart to a mixture of **II-1** (5.63 g, 22.7 mmol) in 50 mL Et_2O. The mixture was stirred and monitored by TLC until the observation of complete consumption of the starting material (usually in 4 hr). Upon completion, the mixture was filtered, solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica; 1:9 v/v ethyl acetate:hexanes) to afford (2,5-dipropyloxyphenyl)acetylene (4.35 g, 88%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.01 (t, ^3J = 7 Hz, 3 H, CH_3), 1.04 (t, ^3J = 7 Hz, 3 H, CH_3), 1.70-1.87 (m, 4H, CH_2), 3.23 (s, 1H, ≡C-H), 3.82 (t, ^3J = 7 Hz, 2 H, OCH_2), 3.92 (t, ^3J = 7 Hz, 2 H, , OCH_2), 6.78 (d, ^3J = 9 Hz, 1H, Ar-6H), 6.83 (dd, ^4J = 3 Hz, ^3J = 9 Hz, 1 H, Ar-5H), 6.97 (d, ^4J = 3 Hz, 1H, Ar-3H). ^{13}C NMR ($CDCl_3$): δ 10.4 (CH_3), 22.5 (CH_2), 70.1 (OCH_2), 71.0 (OCH_2), 80.0 (≡C-H), 80.8 (-C≡), 112.2 (Ar C-4), 113.8 (Ar C-1), 116.9 (Ar C-6), 119.2 (Ar C-3), 152.5 (1C, C-5), 154.5 (C-2). IR (AT-IR, neat): 3284, 2962, 2934, 2875, 2106, 1495, 1466, 1221, 977. MS (EI): m/z (%) 218.1 (100)[M^+], 176.1 (25)[M^+-C_3H_7]. HRMS calculated for $C_{14}H_{18}O_2$, 218.13068; found 218.13463, Δ= 7.6 ppm.

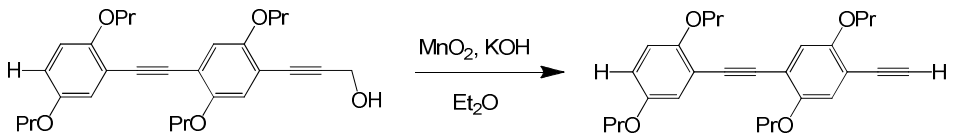


II-3: 43%

1-(4-Iodo-2,5-dimethoxyphenyl)propyn-3-ol, II-3. Propargyl alcohol (900 μL, 15.6 mmol) was added in dropwise to a solution of 1,4-diiodo-2,5-dipropoxybenzene (5.00 g, 15.6 mmol), $Pd(Ph_3P)Cl_2$ (109 mg, 0.156 μmol), CuI (59.4 mg, 0.312 μmol) in 50 mL 1:1 mixture of THF and piperidine under Ar. The reaction mixture was stirred for 12 h, Et_2O (100 mL) was added. And the solution was washed with sat. aq. NH_4Cl (100 mL), and H_2O. The solvent was removed under reduced pressure and the residue was the residue was subjected to column chromatography (silica; 25:75 v/v ethyl acetate:hexanes) to afford the title compound (2.52 g, 43% yield) as a yellow crystalline solid. m.p. = 54-56 ºC; ^{1}H NMR ($CDCl_3$): δ 1.04 (t, ^3J = 8 Hz, 3 H, CH_3), 1.07 (t, ^3J = 8 Hz, 3 H, CH_3), 1.75-1.88 (m, 4H, CH_2), 3.89 (t, ^3J = 7 Hz, 2 H, OCH_2), 3.92 (t, ^3J = 7, 2 H, OCH_2) 4.43 (s, 2H, CH_2OH), 6.74 (s, 1 H, Ar-H), 7.19 (s, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 10.3 (CH_3), 10.6 (CH_3), 22.4 (CH_2), 22.5 (CH_2), 51.6 (CH_2OH), 71.3 (OCH_2), 71.4 (OCH_2), 81.5 (Ar-C≡), 87.7 (≡C), 92.0 (Ar C-4), 112.8 (Ar C-1), 116.2 (Ar C-6), 123.8 (Ar C-3), 151.64 (Ar C-5), 154.1 (Ar C-2). IR (AT-IR, neat): 3511, 2964, 2876, 1465, 1371, 1207, 733 cm^{-1}. MS (EI): *m*/*z* (%) 374.1 (100)[M^+], 332.4 (15)[$-C_3H_7$]. HRMS calculated for $C_{15}H_{19}O_3I$, 374.03790; found 374.03765, Δ = 0.7 ppm.

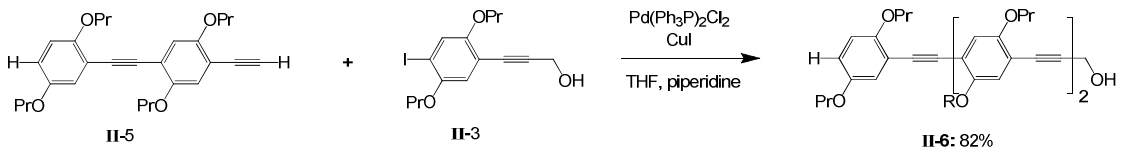


1-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropoxyphenyl)propyn-3-ol, II-4. A mixture of **II-3** (2.00 g, 5.34 mmol), **II-2** (2.33 g, 10.7 mmol), $Pd(Ph_3P)Cl_2$ (38 mg, 50 μmol) and CuI (20 mg, 100 μmol) in 50 mL 1:1 THF and piperidine was stirred for 12 h under Ar. Et_2O (100 mL) was added and the solution was washed with sat. aq. NH_4Cl (100 mL), and H_2O (100 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (25:75 v/v ethyl acetate:hexanes) to afford the title compound (1.55 g, 75% yield) as a yellow crystalline solid. m.p. = 63-65 ºC. ^{1}H NMR ($CDCl_3$): δ 0.99-1.09 (m, 12 H, CH_3), 1.74-1.89 (m, 8H, CH_2), 3.87 (t, ^3J = 7 Hz, 2 H, OCH_2), 3.92-4.00 (m, 6 H, OCH_2), 4.52 (s, 1 H, ≡C-CH_2), 4.54 (s, 1 H, ≡C-CH_2), 6.81-6.83 (m, 2 H, Ar-H), 6.90 (s, 1 H, Ar-H), 6.97 (s, 1 H, Ar-H), 7.01 (m, 1 H, Ar-H). ^{13}CNMR ($CDCl_3$): δ 10.4 (CH_3), 10.5 (CH_3), 10.5 (CH_3), 10.5 (CH_3), 10.6 (CH_3), 22.4 (CH_2), 22.5 (CH_2), 22.6 (CH_2), 22.7 (CH_2), 51.8 (CH_2OH), 70.2 (OCH_2), 71.0 (OCH_2), 71.1 (OCH_2), 71.3 (OCH_2), 82.1 (≡C), 89.5 (≡C), 91.5 (≡C), 92.4 (≡C), 112.8 (Ar), 113.8 (Ar), 114.2 (Ar), 114.8 (Ar), 116.6 (CH-Ar), 117.2 (CH-Ar), 117.6 (CH-Ar), 118.5 (CH-Ar), 152.7 (CO-Ar), 153.3 (CO-Ar), 153.4 (CO-Ar), 153.9 (CO-Ar). IR (AT-IR, neat): 3399, 2961, 2933, 2874, 2219, 1602, 1503, 1467, 1385, 1269, 1201, 1016; MS (EI): *m*/*z* (%) 464.2 (100)[M^+], 435.3 (25), 43.2 (25)[M^+-C_3H_7]. HRMS calculated for $C_{29}H_{36}O_5$, 464.25627; found 464.25551, Δ = 1.6 ppm.

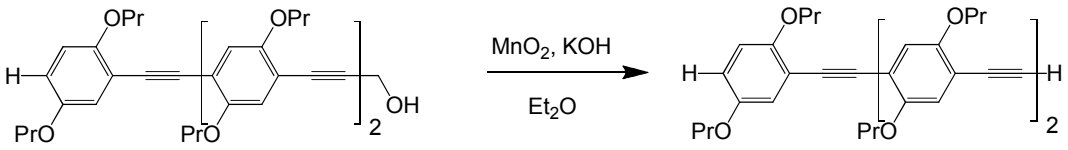


II-4 **II-5:** 88%

(4-(2,5-Dipropyloxyphenylethynyl)-2,5-di-propyloxyphenyl)acetylene, II-5. MnO_2 (3.74 g 43.1 mmol) and crushed KOH (2.37 g, 43.1 mmol) was added in four separate portions to a solution of **II-4** (2.00 g 4.31 mmol) in 45 mL Et_2O. The reaction was monitored by TLC until the starting material was observed to go to complete conversion. The product mixture was then filtered and the solvent removed under reduced pressure to afford the title compound (1.65 g, 88%) as yellow crystals. m.p.= 54-56 ºC. ^{1}H NMR ($CDCl_3$): δ 0.99-1.09 (m, 12 H, CH_3), 1.72-1.90 (m, 8 H, CH_2), 3.32 (s, 1H, ≡C-H), 3.86 (t, ^3J = 7 Hz, 2 H, OCH_2), 3.94-4.00 (m, 6 H, OCH_2), 6.82 (s, 1 H, Ar-H), 6.83 (s, 1 H, Ar-H), 6.97 (s, 1 H, Ar-H), 7.00 (s, 1 H, Ar-H), 7.02-7.04 (m, Ar-H). ^{13}C NMR ($CDCl_3$): δ 10.1 (CH_3), 10.2 (CH_3), 10.3 (CH_3), 10.4 (CH_3) (CH_3), 22.2 (CH_2), 22.3 (CH_2), 22.4 (CH_2), 22.5 (CH_2), 69.8 (OCH_2), 70.6 (OCH_2), 70.7 (OCH_2), 70.8 (OCH_2), 79.8 (≡C), 82.2 (≡C), 89.30 (≡C), 91.5 (≡C), 112.1 (Ar), 113.5 (Ar), 113.8 (Ar), 115.0 (Ar), 116.3 (CH-Ar), 116.8 (CH-Ar), 117.7 (CH-Ar), 118.3 (CH-Ar), 152.5 (CO-Ar), 153.0 (CO-Ar), 153.7 (CO-Ar), 153.8 (CO-Ar). IR (AT-IR, neat): 3279, 2961, 2930, 2874, 2103, 1602, 1501, 1197, 978 cm^{-1}. MS (EI): *m*/*z* (%) 434.3 (100)[M^+], 391.2 (5)[M^+-C_3H_7], 266.1 (15), 43 (15)[C_3H_7]. HRMS calculated for $C_{28}H_{34}O_4$, 434.24571; found 434.24550, Δ = 0.5 ppm.

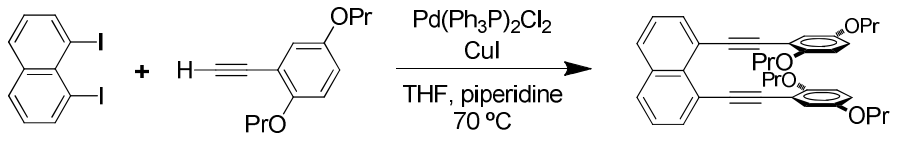


1-(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-di-proyloxyphenyl)propyn-3-ol, II-6. A solution of **II-5** (1.30 g, 2.99 mmol), **II-3** (935 mg, 2.50 mmol), $Pd(Ph_3P)_2Cl_2$ (17.5 mg, 25.0 μmol), and CuI (9.52 mg, 50.0 μmol) in 25 ml 1:1 THF and piperidine under Ar was stirred for 12h. Et_2O (200 mL) was added and the solution was washed with sat. aq. NH_4Cl (200 mL), and H_2O (200 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (25% v/v ethyl acetate:hexanes) to afford the title compound as a green solid (1.40 g, 82% yield). m.p. = 98-100 ºC. ^{1}H NMR ($CDCl_3$): δ 0.99-1.09 (m, 18 H, CH_3), 1.74-1.91 (m, 12 H, CH_2), 2.02 (t, ^3J = 6 Hz, 1 H, -OH), 3.87 (t, ^3J = 6 Hz, 2 H, OCH_2), 3.93-4.01 (m, 10 H, OCH_2), 4.52 (s, 1 H, CH-OH), 4.54 (s, 1 H, CH-OH), 6.81-6.84 (m, 2 H, Ar-H), 6.93 (s, 1 H, Ar-H), 7.00 (s, 1 H, Ar-H), 7.01 (s, 1 H, Ar-H), 7.02 (s, 1 H, Ar-H), 7.03-7.05 (m, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 10.3 (CH_3), 10.4 (CH_3), 10.5 (CH_3), 10.6 (CH_2), 22.4 (CH_2), 22.5 (CH_2), 22.6 (CH_2), 22.7 (CH_2), 51.8 (CH_2OH), 70.1 (OCH_2), 71.0 (OCH_2), 71.1 (OCH_2), 71.1 (OCH_2), 71.3 (OCH_2), 82.0 (≡C), 89.7 (≡C), 91.0 (≡C), 91.5 (≡C), 91.6 (≡C), 92.5 (≡C), 113.0 (Ar), 113.9 (Ar), 114.2 (Ar), 114.6 (Ar), 114.6 (Ar), 116.6 (CH-Ar), 117.1 (CH-Ar), 117.3 (CH-Ar), 117.5 (CH-Ar), 118.5 (CH-Ar), 152.7 (CO-Ar), 153.2 (CO-Ar), 153.3 (CO-Ar), 153.4 (CO-Ar), 153.5 (CO-Ar), 153.9 (CO-Ar). IR (AT-IR, neat): 3435, 2960, 2930, 2867, 2200, 1602, 1495, 1386, 1270, 1203, 1017, 977 cm^{-1}. MS (EI): m/z (%) 680.3 (100)[M+], 637.3 (5)[M^+-C_3H_7]. HRMS calculated for $C_{43}H_{52}O_7$, 680.37130; found 680.36924, Δ = 3.0 ppm.



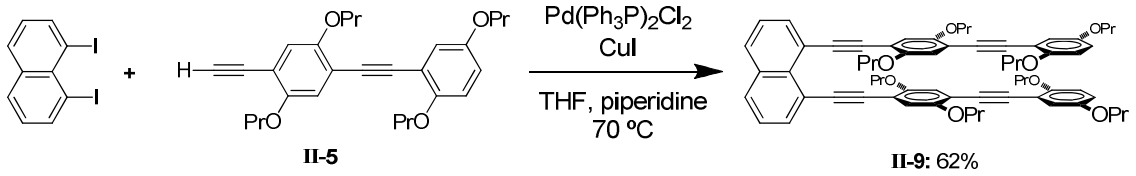
II-6 **II-7:** 83%

(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-di-proyloxyphenyl)acetylene, II-7. MnO_2 (1.66, 19.1 mmol) and KOH (1.05 g 19.1 mmol) were added in four separate portions to a solution of **II-6** (1.30 g 1.91 mmol) in 20 mL Et_2O. The mixture was stirred and monitored by TLC until the observation of complete conversion of the starting material. The reaction mixture was then filtered, solvent removed under reduced pressure, and the residue subjected to column chromatography (1:9 v/v ethyl acetate/hexanes) to afford the title compound as a green solid (1.04 g, 83%). m.p. = 102-104 ºC. ^{1}HNMR ($CDCl_3$): δ 0.99-1.11 (m, 18 H, CH_3), 1.72-1.91 (m, 12 H, CH_2), 3.33 (s, 1 H, ≡C-H), 3.86 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 3.94-4.02 (m, 10 H, -OCH_2-), 6.82-6.83 (m, 2 H, Ar-H), 6.98 (s, 1 H, Ar-H), 7.01 (s, 1 H, Ar-H), 7.02 (s, 1 H, Ar-H), 7.03 (s, 1 H, Ar-H), 7.04-7.05 (m, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 10.4 (CH_3), 10.5 (CH_3), 22.4 (CH_2), 22.5 (CH_2), 22.6 (CH_2), 70.1 (OCH_2), 70.9 (OCH_2), 71.0 (OCH_2), 71.1 (OCH_2), 71.2 (OCH_2), 71.3 (OCH_2), 80.0 (≡C), 82.2 (≡C), 89.7 (≡C), 91.0 (≡C), 91.6 (≡C), 112.5 (Ar), 113.8 (Ar), 113.9 (Ar), 114.2 (Ar), 114.7 (Ar), 114.8 (Ar), 116.6 (CH-Ar), 117.0 (CH-Ar), 117.3 (CH-Ar), 117.4 (CH-Ar), 118.0 (CH-Ar), 118.5 (CH-Ar), 152.7 (CO-Ar), 153.2 (CO-Ar), 153.3 (CO-Ar), 153.4 (CO-Ar), 153.9 (CO-Ar), 154.0 (CO-Ar). IR (AT-IR, neat): 3282, 3259, 2957, 2930, 2904, 2870, 2153, 1598, 1505, 1422, 1386, 1200, 1021, 858 cm^{-1}. MS (EI): m/z (%) 650.4 (100)[M+], 621.4 (10). HRMS calculated for $C_{42}H_{50}O_6$, 650.36074; found 650.36531, Δ = 7.0 ppm.



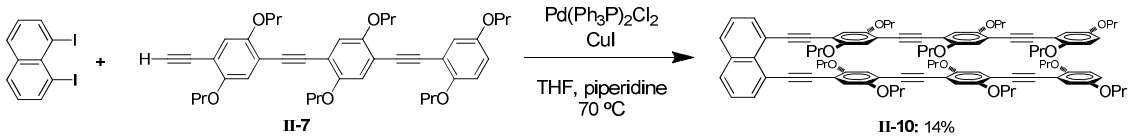
II-2 **II-8:** 65%

1,8-(2,5-Dipropyloxyphenylethynyl)naphthalene, II-8. A solution of 1,8-diiodonaphthalene (500 mg, 1.32 mmol), **II-2** (717 mg, 3.30 mmol), $Pd(Ph_3P)Cl_2$ (23 mg, 33 μmol) and CuI (13 mg, 66 μmol) in 30 ml 1:1 THF and piperidine under Ar was stirred at 70 ºC for 12 h. Et_2O (100 mL) was added and washed with sat. NH_4Cl (100 mL), and H_2O (100 mL). The solvent was removed under reduced pressure and the residue subjected to column chromatography (5:95 v/v ethyl acetate:hexanes) followed by recrystallization from methanol to give the title compound as a beige solid (482 mg, 65% yield). m.p. = 79-80 ºC. ^{1}H NMR ($CDCl_3$): δ 0.91 (t, ^3J = 7 Hz, 6 H, CH_3), 1.08 (t, ^3J = 7 Hz, 6 H, CH_3), 1.55-1.67 (m, 4 H, CH_2), 1.80-1.92 (m, 4 H, CH_2), 3.37 (t, ^3J = 7 Hz, 4 H, OCH_2) 3.89 (t, ^3J = 7 Hz, 4 H, OCH_2), 6.72-6.75 (m, 4 H, Ar-H), 6.78-6.82 (m, 2 H, Ar-H), 7.47 (dd, ^3J = 7 Hz, ^3J = 7 Hz, 2 H, naphthyl H3, 6), 7.81 (dd, ^4J = 1 Hz, ^3J = 7 Hz, 2 H, napthyl-H), 7.88 (dd, ^4J = 1 Hz, ^3J = 7 Hz, 2 H, napthyl-H). ^{13}C NMR ($CDCl_3$): δ 10.7 (CH_3), 10.9 (CH_3), 22.8 (CH_2), 23.0 (CH_2), 69.7(OCH_2), 71.3 (OCH_2), 93.9 (C≡C), 94.1 (C≡C), 113.8, 114.3, 117.1, 117.8, 121.7, 125.8, 129.5, 131.4, 134.3, 135.0, 152.8 (CO-Ar), 154.3 (CO-Ar). IR (AT-IR, neat): 2957, 2930, 2870, 2359, 2196, 1595, 1495, 1216, 978 cm^{-1}. MS (EI): m/z (%) 560.3 (100)[M+], 517.3 (60)[M^+-C_3H_7]. HRMS calculated for $C_{38}H_{40}O_4$, 560.29029; found 560.29266, Δ = 4.2 ppm. Elem. Anal. calcd. C 81.45, H 7.20, O 11.42; found C 81.36, H 7.26, O 11.52.



1,8-(4- (2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)naphthalene, II-9. A solution of 1,8-diiodonaphthalene **(**500 mg, 1.32 mmol), **II-5** (1.25 g, 2.88 mmol), $Pd(Ph_3P)_2Cl_2$ (20 mg, 20 μmol), and CuI (11 mg, 58 μmol) in 26 ml 1:1 THF and piperidine under Ar was stirred at 70 ºC for 12 hr. Et_2O (100 ml) was added and washed with sat. NH_4Cl (100 ml), and water (100 ml). The solvent was removed under vacuum and the residue subjected to column chromatography (1:9 v/v ethyl acetate:hexanes). After removing the solvent, the residue was triturated with hexanes and methanol to give the title compound as a green solid (810 mg, 62% yield). m.p. = 45-48 ºC. ^{1}H NMR ($CDCl_3$): δ 0.96-1.14 (m, 24 H, CH_3), 1.65-1.95 (m, 16 H, CH_2), 3.44 (t, ^3J = 6 Hz, 4 H, OCH_2), 3.86 (t, ^3J = 6 Hz, 4 H, OCH_2), 3.94 (t, ^3J = 6 Hz, 4 H, OCH_2), 3.97 (t, ^3J = 6 Hz, 4 H, OCH_2), 6.79-6.82 (m, 4 H, Ar-H), 6.84 (s, 2 H, Ar-H), 6.99 (s, 2 H, Ar-H), 7.01-7.02 (m, 2 H, Ar-H), 7.48 (dd, ^3J = 7 Hz, ^3J = 7 Hz, 2 H, naphthyl-H 3,6), 7.83 (dd, ^4J = 1 Hz, ^3J = 7 Hz, 2 H, naphthyl-H), 7.90 (dd, ^4J = 1 Hz, ^3J = 7 Hz, 2 H, naphthyl-H). ^{13}C NMR ($CDCl_3$): δ 10.4 (CH_3), 10.5 (CH_3), 22.5 (CH_2), 22.7 (CH_2), 70.1 (OCH_2), 70.3 (OCH_2), 70.8 (OCH_2), 71.4 (OCH_2), 89.9 (≡C), 91.4 (≡C), 93.7 (≡C), 95.6 (≡C), 114.1, 114.2, 114.3, 116.5, 116.6, 118.5, 121.2, 125.6, 129.4, 130.9, 134.0, 134.9, 152.8 (CO-Ar), 153.3 (CO-Ar), 153.5 (CO-Ar), 153.9 (CO-Ar). IR (AT-IR, neat): 3046, 2960, 2930, 2870, 2196, 1598, 1495, 1270, 1193, 977, 761 cm^{-1}. MS (MALDI): m/z (%) 992.6

(100)[M+], 951.5 (60). HRMS found 992.5227, Δ = 15 ppm for $C_{66}H_{72}O_8$; Elem. Anal. calcd. C 79.81, H 7.30, O 12.89; found C 79.88, H 7.40, O 12.77.



1,8-(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-diproyloxyphenylethynyl)naphthalene, II-10. A solution of **II-7** (800 mg, 1.23 mmol), 1,8-diiodonaphthalene (200 mg, 0.526 mmol), $Pd(Ph_3P)_2Cl_2$ (7.40 mg, 10.5 μmol), and CuI (4.00 mg, 21.0 μmol) 11 mL 1:1 THF and piperidine under Ar was stirred at 70 ºC for 12 h. Et_2O (100 mL) was added and washed with sat. NH_4Cl (100 mL) and water (100 mL). The solvent was removed under reduced pressure and residue subjected to column chromatography (2:8 v/v ethyl acetate:hexanes). After removal of the solvent, the residue was triturated with hexanes and methanol to give the title compound as a green solid (210 mg, 14% yield). m.p. = 119-121ºC. ^{1}H NMR ($CDCl_3$): δ 0.97-1.14 (m, 36 H, CH_3), 1.68-1.96 (m, 24 H, CH_2), 3.45 (t, ^3J = 6 Hz, 4 H, OCH_2), 3.88 (t, ^3J = 6 Hz, 4 H, OCH_2), 3.92-4.01 (m, 16 H, OCH_2), 6.82-6.83 (m, 4 H, Ar-H), 6.85 (s, 2 H, Ar-H), 6.99 (s, 2 H, Ar-H), 7.01 (s, 2 H, Ar-H), 7.02 (s, 2 H, Ar-H), 7.03-7.04 (m, 2 H, Ar-H), 7.48 (dd, 2 H, ^3J = 7 Hz, ^3J = 7 Hz, 2 H, naphthyl H3, 6), 7.84 (dd, ^4J = 1 Hz, ^3J = 7 Hz, 2 H, naphthyl-H), 7.91 (dd, ^4J = 1 Hz, ^3J = 7 Hz, 2 H, naphthyl-H). ^{13}C NMR ($CDCl_3$): δ 10.4 (CH_3), 10.5 (CH_3), 22.5 (CH_2), 22.6 (CH_2), 22.7 (CH_2), 70.1 (OCH_2), 70.3 (OCH_2), 70.9 (OCH_2), 71.1 (OCH_2), 71.3 (OCH_2), 89.8 (≡C), 91.4 (≡C), 91.5 (≡C), 93.7 (≡C), 95.8 (≡C), 113.8, 113.9, 114.1, 114.2, 114.4, 116.5, 117.3, 117.4, 118.5, 121.2, 125.6, 134.0, 135.0, 152.7

(CO-Ar), 153.3 (Co-Ar), 153.5 (CO-Ar), 153.9 (CO-Ar). IR (AT-IR, neat): 3050, 2960, 2930, 2870, 2196, 1602, 1499, 1266, 1207, 981 cm^{-1}. MS (MALDI): m/z (%) 1424.7; HRMS found 1424.742, Δ = 10 ppm for $C_{94}H_{104}O_{12}$. Elem. Anal. calcd. C 79.18, H 7.35, O 13.47; found C 79.12, H 7.39, O 13.44.

2.3. Results and Discussion

2.3.1. Synthesis of Oligo(1,4-Phenylene Ethynylene)s

PE oligomers with up to three repeat units were synthesized in a multi-step synthesis using Sonogashira coupling of appropriately substituted phenyl acetylenes to aryl iodides, Figure 2.1. This synthetic scheme made use of propargyl alcohol as a polar protecting group for the alkyne which allowed for the isolation of gram-quantities of oligomers without laborious purifications.

1,4-Dipropyloxybenzene was iodinated upon treatment with molecular iodine in the presence of potassium periodate with a catalytic amount of H_2SO_4 added to methanol solvent. The quantity of iodine was adjusted to give either mainly mono- or di-iodinated product. Optimized attempts to make mono-iodinated product **II-1b** gave a mixture that contains approximately 10-15% of diiodinated product (by integration of ^1H NMR signals of the crude product mixture). This was not removed, and the mixture was subjected to Sonogashira coupling conditions with an excess of propargyl alcohol. Upon workup, the product mixture was simple to separate by column chromatography to afford pure mono-propargyl alcohol product **II-1b**. Conversion of the propargyl alcohol to the alkyne **II-2** was done under oxidative conditions with manganese (IV)oxide and potassium hydroxide in dry ether, oftentimes requiring no additional purification. **II-2**

serves as the "tail" of the oligomers. Treatment of 1,4-diiodo-2,5-dipropyloxybenzene with 0.5 equivalents propargyl alcohol gave a bi-functional compound, **II-3**. Alkynes **II-2** and **II-5** were coupled to iodide **II-3** to add one PE repeat unit and afford alcohols **II-4** and **II-6**. The alcohol again facilitated purification upon oxidation to give alkynes **II-5** and **II-7** respectively.

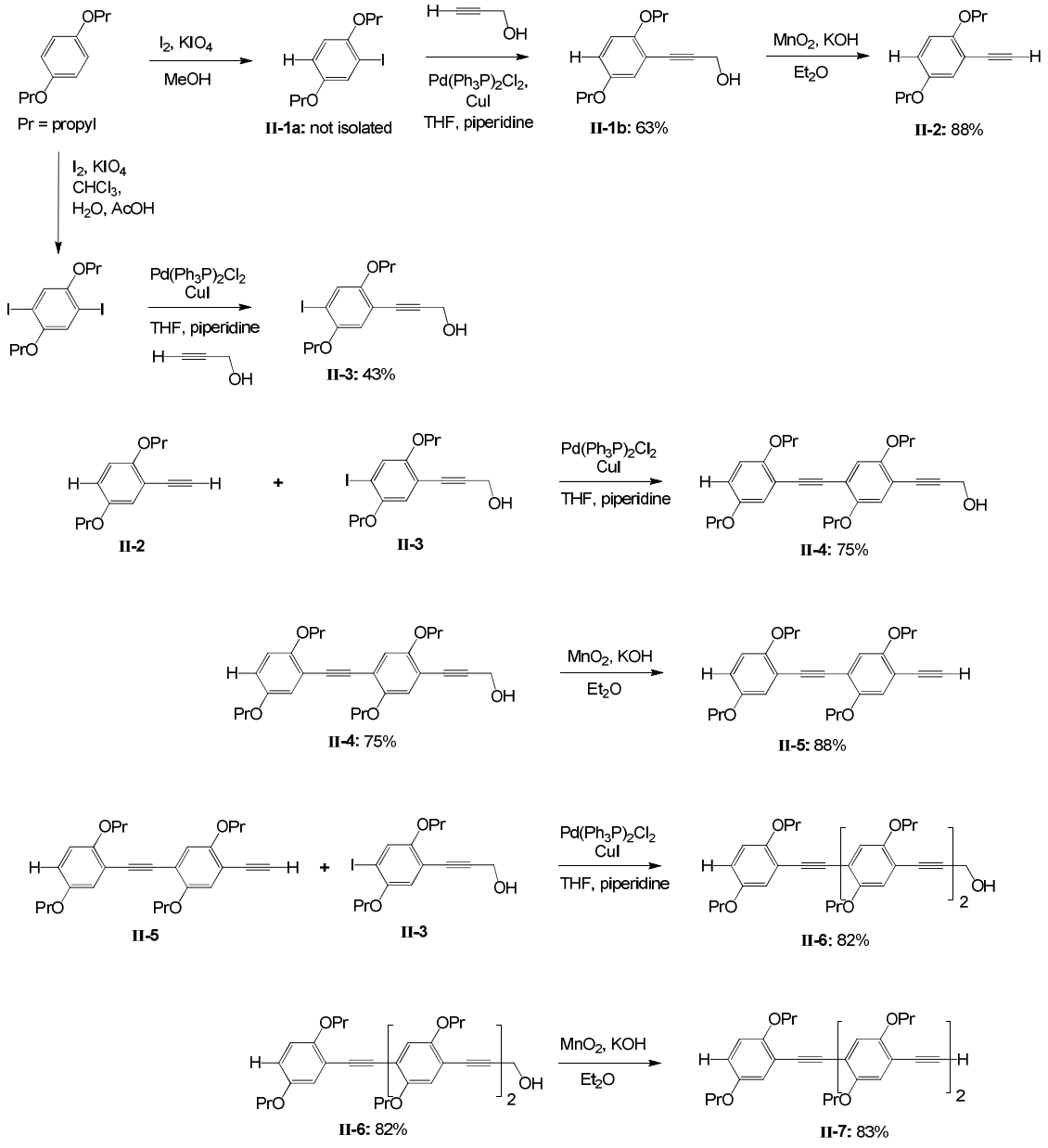


Figure 2.1. Synthesis of oligomer PE arms and subsequent coupling to 1,8-diiodonapthalene.

2.3.2. Preparation of Diiodonaphthalene and Coupling of Oligo(PE) Arms

1,8-Diiodonaphthalene was prepared in one step from commercially available 1,8-diaminonaphthalene (Aldrich) following the procedure originally reported by House.[41] This reaction proceeds by diazotization with sodium nitrite in dilute acid followed by displacement with potassium iodide. The reaction proceeds at 0 ºC and is highly exothermic. One of the major challenges from this reaction is extraction and isolation of the product from organic byproducts and inorganic salts. This requires the product be subjected to recrystallization and chromatography to obtain purified product suitable for coupling reactions.

Coupling of alkynes **II-2**, **II-5**, and **II-7** to 1,8-diiodonaphthalene proceeded using Sonogashira reaction conditions[52] under argon at 70 ºC, as shown in Figure 2.2. Attempts to couple alkynes at lower temperature lead to significant quantities of the intermediate mono-substituted product. Additional thermal energy is required to overcome the strain associated with coupling of the second alkyne. Despite the exclusion of air, formation of some homo-coupled 1,3-di-yne product was formed. This was removed with column chromatography which after removal of the solvent, the product was further triturated in methanol and hexanes to afford **II-8-10**.

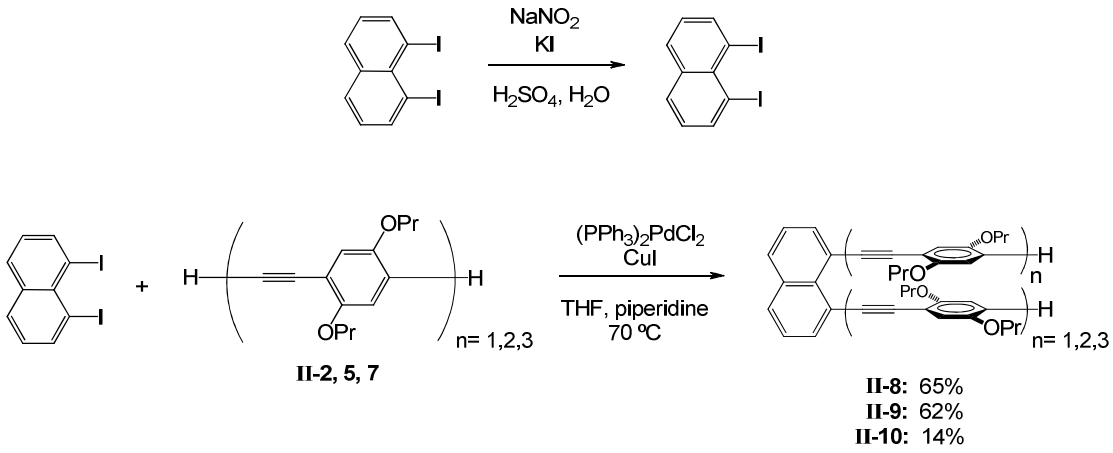


Figure 2.2. Preparation of 1,8-diiodonaphthalene and subsequent coupling of PE oligomers.

2.3.3. Structural Characterization: ^{1}H NMR and ^{13}C NMR Spectroscopy

All compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR of the reaction mixture formed upon attempts to mono-iodinate 1,4-dipropyloxy benzene is shown in Figure 2.3. The aromatic protons between δ 6.5–7.5 ppm showed a doublet, a doublet of doublets, and a doublet, consistent with a 1,3,5-substituted benzene; along with a singlet for the di-iodinated product at δ 7.18 ppm and a singlet for the starting material that overlaps with a signal from the mono- at δ 6.74 ppm. Integration of these peaks found the presence of mono- to di-iodinated product and starting material in an approximate ratio of 88:10:2, respectively. This same splitting pattern was found for all compounds in the synthesis that contained the 1, 3, 5-trisubstituted benzene.

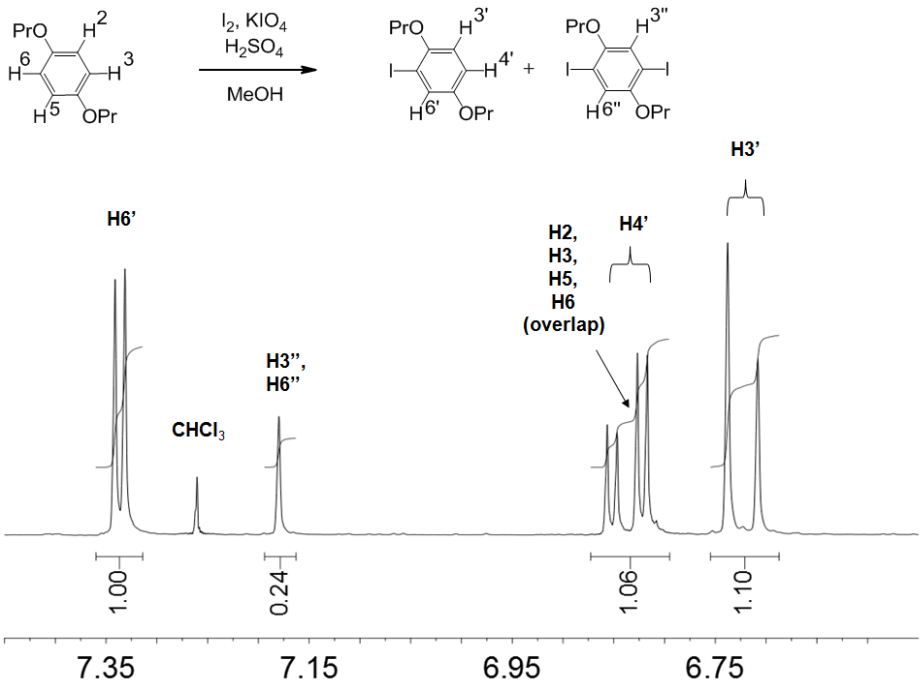


Figure 2.3. [1]H NMR of the crude product mixture of **II-1a**. Peaks are assigned to protons of the products and integration shows relative abundance of all components.

In the ^{1}H NMR of the naphthalene-bridged trimer **II-10**, Figure 2.4, the presence of dissimilar alkyl groups resulted in many overlapping peaks with chemical shifts from δ 0.8 to 4.2 ppm. However, the aromatic region from δ 6.5 to 8.0 ppm provides evidence for the formation of the desired product. The presence of four singlets indicates the presence of two types of asymmetrically tetra-substituted phenylenes. These singlets were shifted upfield from the unsubstituted alkyne **II-7**, consistent with a change in chemical shift anisotropy. Furthermore, there is a doublet of doublets at δ 7.5 ppm and two sets of doublets of doublets at δ 7.8 and δ 7.9 ppm which arise from protons of the symmetrical 1,8-disubstituted naphthalene. The peaks from the protons of the terminal 1, 3, 5-substituted benzene appear as a multiplet. All molecules were also analyzed by mass spectrometry and infrared spectroscopy. Elemental analysis supported the formation of the final products **II-8-10**.

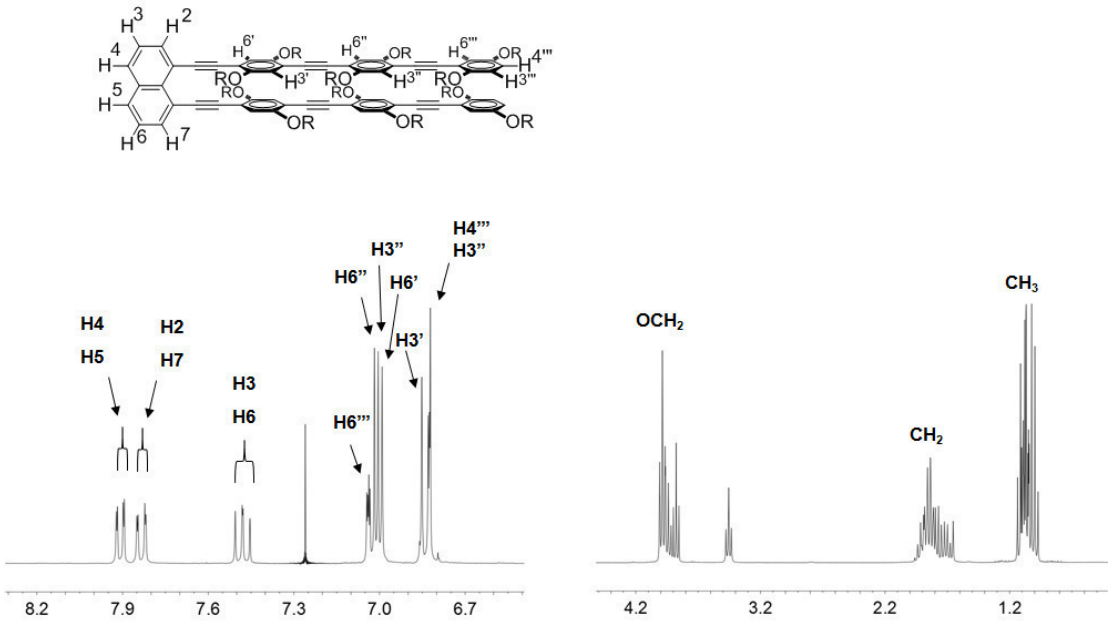


Figure 2.4. ^{1}H NMR (300 MHz) of **II-10**. Note the two regions are not on the same y-scale.

2.3.4. X-ray Structural Analysis

Naphthalene-bridged oligo(PE) **II-8** was crystallized by slow solvent evaporation from 10:90 ethyl acetate:hexanes over 12 h at room temperature. We collected single crystal X-ray structures to explore the interactions of the naphthyl-bridged oligo(PE)s bearing di-alkoxy side chains, Figure 2.5. The dialkoxy phenylenes afforded a twisted-geometry where the phenylene rings lie out of plane. The angle of C14-C18-C32 is 142º (Figure 2.5 A), where this angle would be 90º in a completely co-facial orientation. This splaying results in the C16 and C30 atoms of the two phenylene rings to be 6.7 Å apart. Other measurements that characterize the deformations to the naphthalene are the C1-C9-C27 angle of 102º (Figure 2.5 B) and the C4-C1-C13 angle of 165º (Figure 2.5 C), which were expected to be ca. 90º and 180º, respectively if these deformations were not present. This identifies that there is a substantial amount of strain on the naphthalene moiety resulting in structures in which the oligomers are not in a stacked orientation.

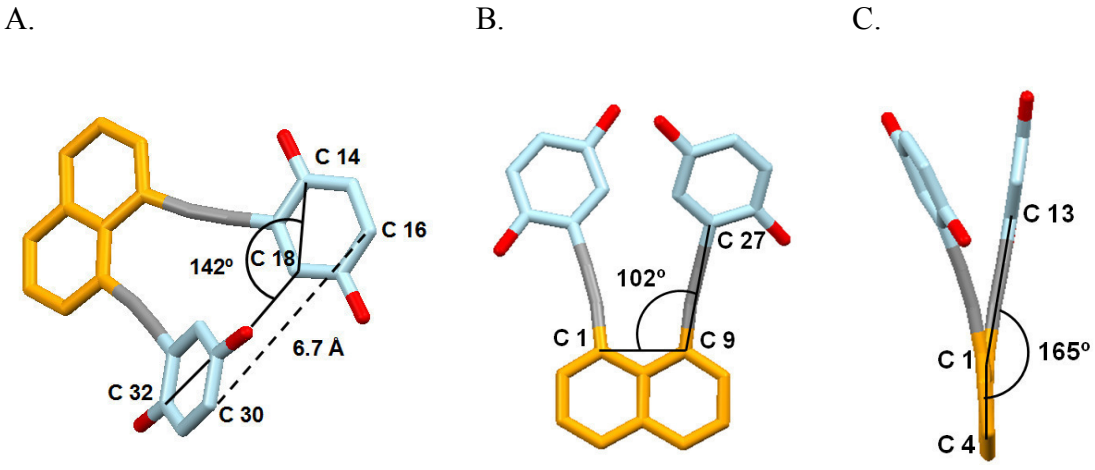


Figure 2.5. Molecular structure of X-ray crystal structure of naphthalene-bridged PE, **II-8**. Propyl groups are omitted for clarity.

The packing of naphthyl-bridged PE **II-8** is shown in Figure 2.6. The unit cell is P2 sub 1c where two of the naphthalenes are pointing in the same direction but not in the same plane so that the alkyne arms are interdigitated. Figure 2.6 A illustrates that the C16-C30 intermolecular bond angles in the unit cell are 7.6 Å apart. C5 Atoms amongst two adjacent naphthalenes are 9.1 Å apart from one another and interestingly, the C16 and C30 of two adjacent phenylenes are 4.8 Å apart from one another which suggests that some interaction of the phenylene units plays a role in ordering in the unit cell.

A. B. C.

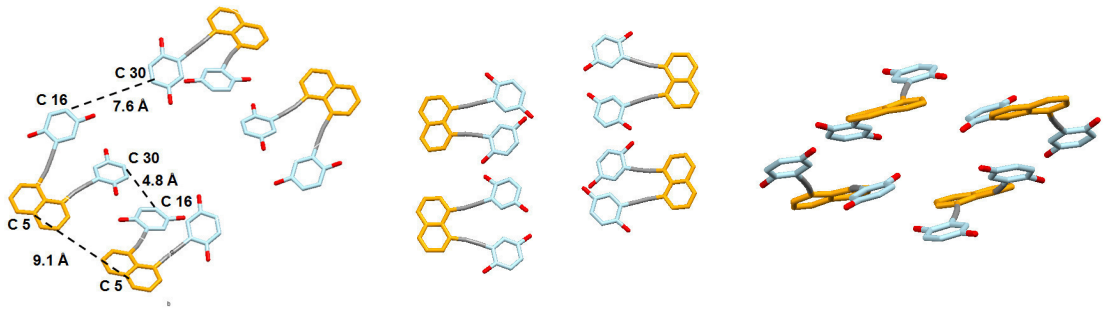


Figure 2.6. Crystal packing structure of naphthyl-bridged PE, **II-8**. Propyl groups are omitted for clarity.

2.3.5. Electrochemistry of Naphthalene-Bridged and Unbridged Oligo(PE)s

Interest in the electronic structure of PE oligomers and polymers prompted a study of the electrochemical properties of these compounds. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed, and data are given in Table 2.1 and 2.2, and Figures 2.7 and 2.8.

Cyclic voltammograms of **II-7-10**, are shown in Figure 2.7. Of the three linear unbridged oligo PEs **II-2**, **5**, and **7**, only the trimer **II-7** was found to have an irreversible one-electron oxidation with a peak potential of +1.74 V. However, all of the naphthalene-bridged PE oligomers undergo quasi-reversible oxidations. Each of these compounds display a splitting of the oxidation wave. For example, naphthyl-bridged monomer **II-8** shows onset of oxidation at +1.59 V with a peak at +1.77 V. A second oxidation takes place at +1.96 V. Analysis of the oxidations by DPV in Figure 2.8 supported these measurements. A comparison of **II-8-10** found that as the conjugation length of the PE oligomer increases, there is a lowering of both the first- and second- electron oxidation potentials as shown in Figure 2.9. A linear trend from a plot of these potentials with the reciprocal number of PE repeat units is also given in Figure 2.9.

Table 2.1. Electrochemical CV data for alkyne **II-7** and naphthyl-bridged PE oligomers **II-8-10**.

	Potential / (+)V			
Compound	I_{ox}	II_{ox}	I_{red}	II_{red}
II-8	1.77	1.96	1.58	1.38
II-9	1.63	1.76	1.63	1.32
II-7	1.71	-	-	-
II-10	1.56	1.70	1.58	1.33

Table 2.2. Electrochemical DPV data for alkyne **II-7** and naphthyl-bridged PE oligomers **II-8-10**.

	Potential / (+)V	
Compound	I_{ox}	II_{ox}
II-8	1.74	1.92
II-9	1.63	1.77
II-7	1.71	-
II-10	1.57	1.70

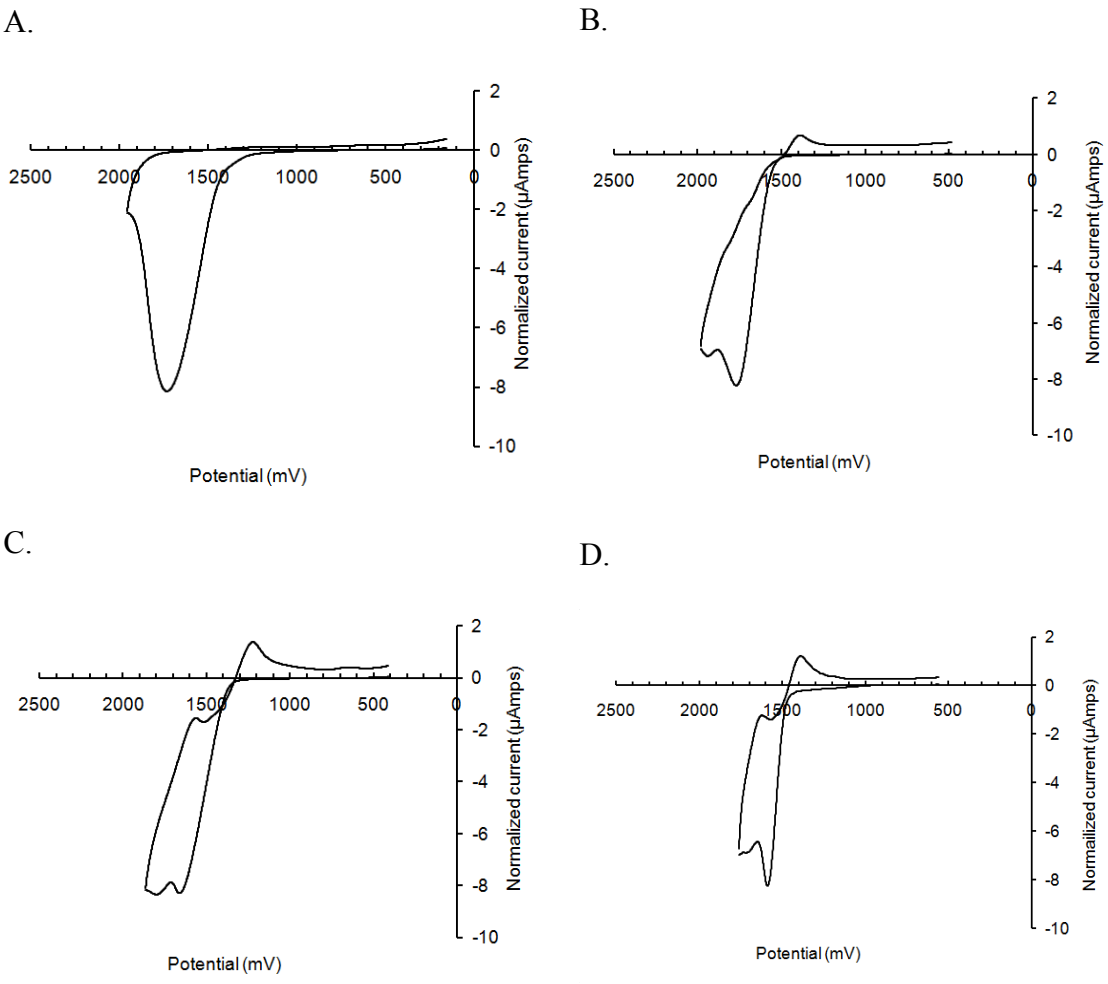


Figure 2.7. CV measurements of naphthalene-bridged compounds (a) **II-7**, b) **II-8**, c) **II-9**, d) **II-10** in CH_2Cl_2 with 0.1 M nBu_4PF_6. Scans were made at 100 mV/sec using a gold working electrode and silver reference electrode with samples referenced to Fc/Fc^+ at 450 mV.

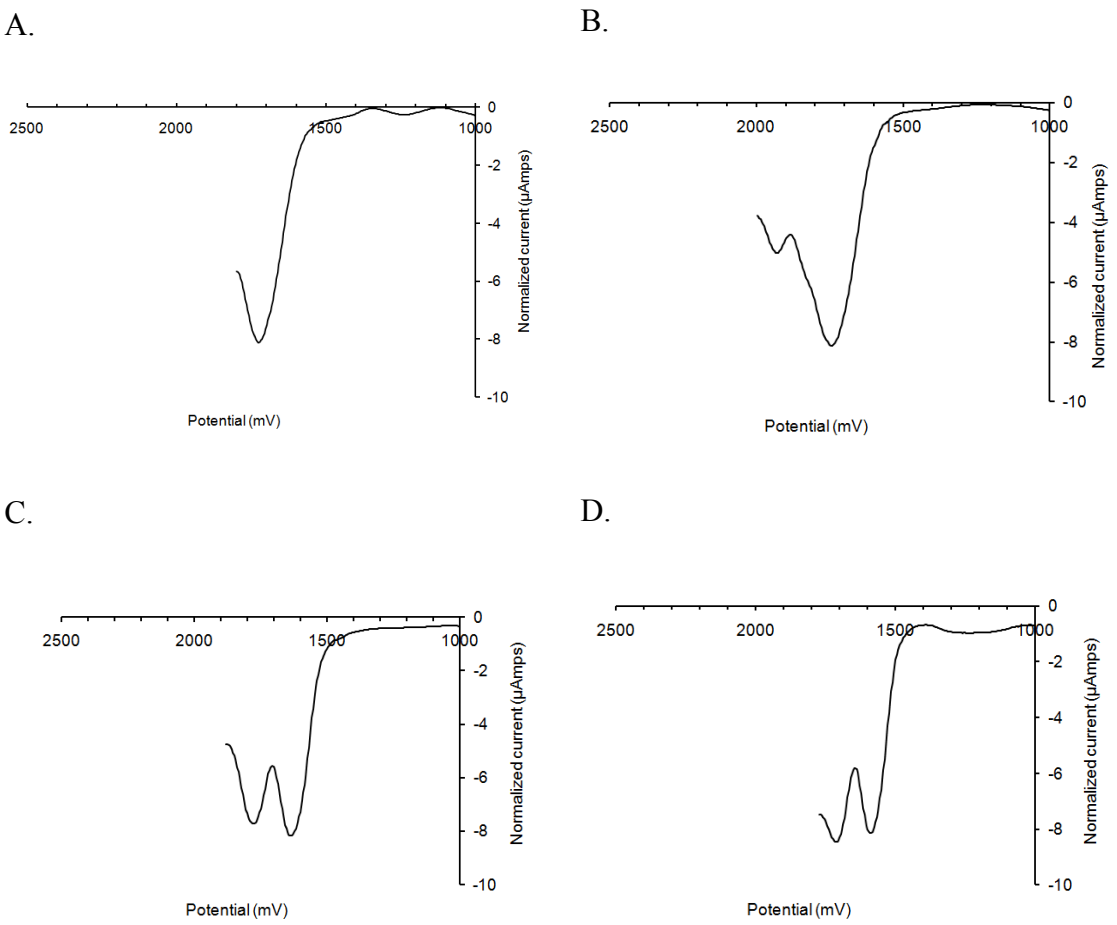


Figure 2.8. DPV measurements of naphthalene-bridged oligo(PE)s (a) **II-7**, b) **II-8**, c) **II-9**, d) **II-10** in CH_2Cl_2 with 0.1 M nBu_4PF_6. Scans were made using a gold working electrode and silver reference electrode with samples referenced to Fc/Fc^+ at 450 mV.

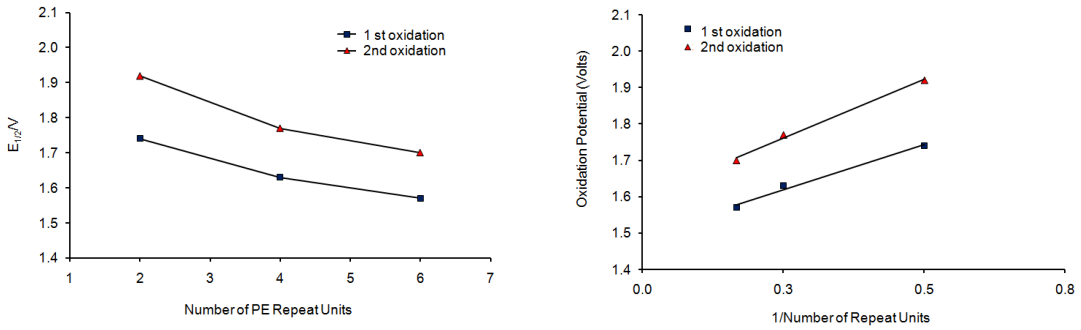


Figure 2.9. Plots that resolve the decrease in potential required for one- and two-electron oxidation of the naphthyl-bridged oligo(PE)s **II-8-10** with respect to the number of PE repeat units in the structure (left) and with the inverse number of repeat units (right).

The 1,8-naphthalene unit that binds the PE oligomers disrupts the linearity and complete planarization of the molecule as a whole. Despite this it appears that the difference between the first and second oxidation potentials are greater than 0.1 V apart which is very similar to the thiophene oligomers reported by Tour.[53] Therefore, it appears that the conjugation is continuous through the naphthalene unit and the entire molecule is acting as a single electrophore where there are no intramolecular electronic effects that can be attributed to π-stacking.

2.3.6. UV-vis and Fluorescence Measurements of Linear Oligo PEs and Naphthalene-Bridged Analogs.

Naphthalene-bridged oligomers resemble segments of conjugated polymer chains which are closely packed in the solid state. This presented the opportunity to explore the spectroscopic properties of this series of unique π-conjugated structures. The data collected in this study is given in Table 2.3 and Figure 2.10.

Alkynes **II-2**, **5**, and **7** show absorption maxima from 314 to 368 nm where the UV absorption becomes progressively more red-shifted as the number of PE repeat units in the oligomer increases. The alkynes have molar absorptivity values ranging from 4.6×10^3 to 49.6×10^3 $M^{-1}cm^{-1}$ which also increases with the number of PE repeat units.

Naphthyl-bridged PE oligomers **II-8-10** have a λ_{max} of UV absorption that is more red-shifted than the corresponding alkynes that make up their constituents. The naphthyl-bridged monomer **II-8** has a broad absorption at longer wavelength that extends to 425 nm which is not observed with the corresponding dimer and trimer (**II-9** and **10**). Such long wavelength absorptions are often attributed to vibronic coupling.[25] The molar absorptivity of these naphthalene-bridged compounds is more than double the corresponding alkynes with a range of 20.0×10^3 to 105.9×10^3 $M^{-1}cm^{-1}$. Naphthyl-bridged trimer **II-10** has a very broad absorption spectrum due to the extended conjugation with the naphthalene.

The fluorescence spectrum of the naphthyl-bridged PE oligomers **II-8-10** are red-shifted compared to the alkynes **II-2**, **5**, and **7.** Compounds **II-8** and **II-9** are shifted to longer wavelength by more than 50 nm from conjugation extending through the naphthalene. For naphthyl-bridged trimer **II-10** the shift is only 25 nm due to a slight blue-shift of the fluorescence possibly from new chromophore segments within this molecule that are unseen for the other two naphthyl-bridged PEs that are smaller in the series. The unbridged alkynes show progressively increasing Stokes shifts that ranges from 34 to 58 nm. However for the naphthyl-bridged PE oligomers, dimer **II-9** has the largest Stokes shift at 71 nm, which is more than **II-8** and **II-10**. A plot of the Stokes shifts are given in Figure 2.11.

Large Stokes shifts are consistent with molecules that have overlapping π-orbitals such as conjugated oligomers bridged to in [2.2]paracyclophane, [31-32,37-38] However, in this series of naphthalene-bridged PE oligomers, there is minimal π-stacking and the effects from the Stokes shifts must arise from new chromophore units from conjugation with the phenylene ethynylene units and the naphthalene.

Table 2.3. UV-vis absorbance and fluorescence data for alkynes **II-2**, **II-5**, and **II-7** and naphthyl-bridged PE oligomers **II-8-10**.

Monomer /oligo-mer	Number of consecutive phenylene ethynylene rings	$\lambda_{abs\ solution}$ (nm)	Molar absorptivity $\varepsilon /\times 10^3$	$\lambda_{em\ solution}$ (nm)	Stokes shift $\lambda_{abs\ solution}$ (nm) - $\lambda_{em\ solution}$ (nm)
II-2	1	314	4.6	348	34
II-5	2	341	25.8	394	53
II-7	3	368	49.6	426	58
II-8	1	356	20.0	404	48
II-9	2	384	79.7	455	71
II-10	3	398	105.9	451	53

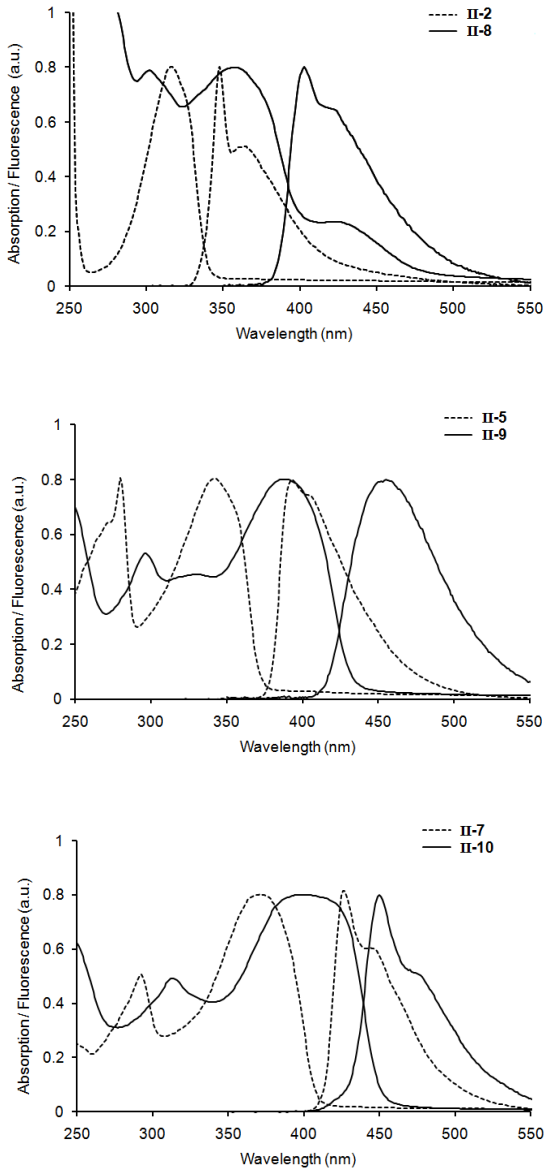


Figure 2.10. UV-vis and fluorescence spectra of unbridged PE oligomers **II-2** (top chart- dashed)**, 5** (middle chart- dashed)**,** and **7** (bottom chart- dashed) and naphthyl-bridged PE oligomers **II-8** (top chart- solid), **II-9** (middle chart- solid), and **II-10** (bottom chart- solid) in dichloromethane at ~10^{-6} M concentration.

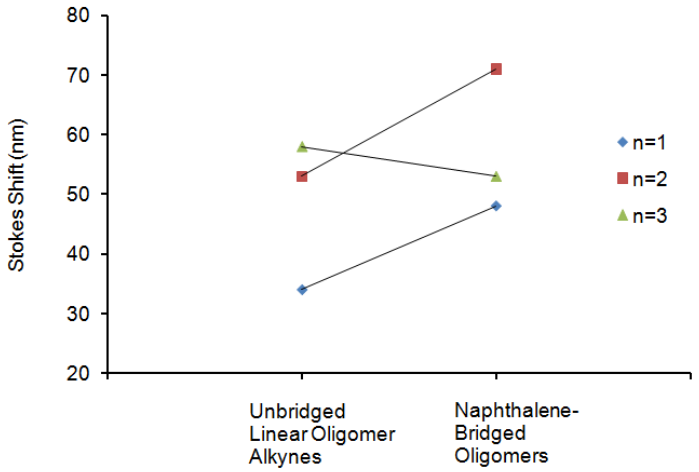


Figure 2.11. Plot of the Stokes shifts for alkynes **II-2**, **5**, and **7** versus the naphthalene-bridged oligomers **II-8**, **9**, and **10**, respectively. The legend corresponds to the number of consecutive PE repeat units.

2.4. Conclusion

We have identified an efficient synthesis of dialkoxy PE oligomers with up to three repeat units by the use of propargyl alcohol functional groups. These oligomers were coupled to 1,8-diiodonaphthalene by Sonogashira coupling. Naphthalene-bridged oligomers show trends in two-electron oxidation which is the same trend as linear conjugated oligomers and red shifts of the UV-absorption and fluorescence spectra compared to the unbridged alkynes. The crystal structure shows strong distortions of the naphthalene unit so that the phenylene units do not demonstrate π-stacking with one another.

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CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF AN OLIGO(1,4-PHENYLENE ETHYNYLENE) TRIAD: A THREE-TIERED OLIGOMER JOINED BY TWO 1,8-SUBSTITUTED NAPHTHALENE BRIDGING UNITS

3.1. Introduction

Organic semiconductors such as pentacene have gained attention as materials for use in thin-film transistors (TFT)s and other electronic devices due to their high field effect mobility which can be upwards of 0.5 $cm^2/V \cdot s$. The high field effect mobility is attributed to π-stacking interactions amongst the oligomers.[1] Therefore, improving the field effect mobility of organic transistors will rely on an understanding and control over such interactions that can be explored through the synthesis of π-stacking models.

1,8-Disubstituted naphthalene is an ideal bridging unit for making π-stacked compounds as it offers geometry where two linear conjugated units can be held parallel to one another with an inter-atomic distance under 3 Å. This presents a possibility for aromatic units to be held in a permanent co-facial orientation so there are superimposable π-interactions. From a synthetic standpoint, naphthalene is an aromatic cycle that can be functionalized with halides at the 1,8- C atoms to couple on different types of conjugated units such as oligo(thiophene)s,[2-3] oligo(phenylene)s,[4-5] imidazoles,[6] and porphyrins.[7-8]

Early reports by House[9-11] established the synthesis and characterization of 1,8-diphenyl naphthalene to show that the phenylene units have an eclipsing conformation as they make up a π-stack. Later work by Nakayama[12] and Iyoda[13] have used

oligo(thiophene)s to show that additional naphthalene units can be incorporated into the structure to produce three- and even four-tiered oligomers, Figure 3.1. Structures that contain multiple π-stacks could have conduction properties similar to the π-dimer conduction bands that have been studied by Miller[14-17] and others[18-20]. Therefore, the need exists to identify and characterize new structures where charge transfer facilitated by π-stacking interactions can take place.

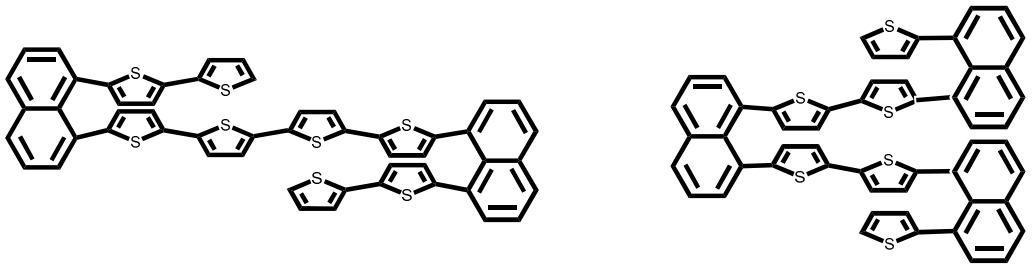


Figure 3.1. Examples of some of the triple- and quadruple- 1,8-dinaphthyl oligo(thiophene)s synthesized by Nakayama[12] (left) and Iyoda[13] (right).

3.2. Experimental

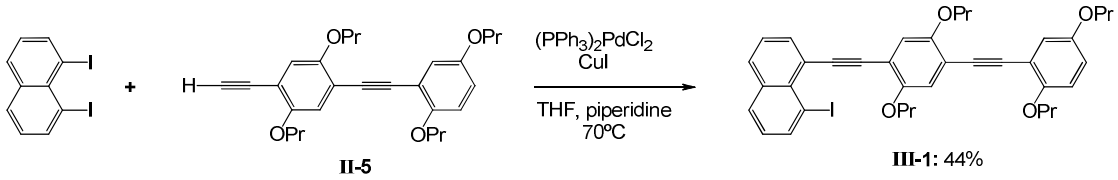
3.2.1. General Procedures

All reactions were conducted with distilled solvents in oven-dried and argon-charged glassware. All reagents were used as received from commercial suppliers without prior purification. Analytical thin layer chromatography (TLC) was performed on pre-coated aluminum-backed plates purchased from Sorbent Technologies (silica gel 60 F254; 0.25 mm thickness). Flash column chromatography was performed on silica gel 60 (230-400 mesh ASTM) from Sorbent Technologies. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer (300 MHz for ^{1}H, 100 MHz for ^{13}C). NMR spectra were measured in solutions of deuterated chloroform ($CDCl_3$) with tetramethylsilane as the internal standard and reported in parts per million (ppm). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet.

IR spectra were collected on a Nicolet 4700 FTIR with an ATR attachment from SmartOrbit Thermoelectronic Corp with samples as neat films. Mass spectra including high resolution were measured by EI on a Waters 70SE instrument or MALDI Micromass TofSpec2E instrument. Elemental analyses were obtained from Atlantic Microlabs in Norcross, Georgia. UV-vis/near-IR was recorded on a Perkin-Elmer Lamda 19 spectrometer. Fluorescence measurements were made on a Shimadzu RF-5301 PC in solutions in dichloromethane at ~10^{-6} M. X-ray Crystal structures were collected on a Bruker Apex-II CCD by Kenneth Hardcastle at Emory University X-ray facility.

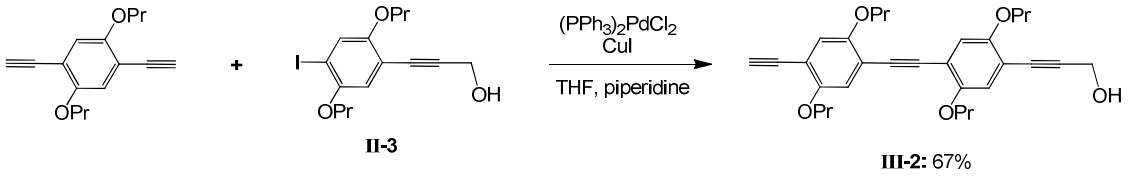
3.2.2. Synthetic Procedures

1,8-Diiodonapthalene,[21] 1,4-diiodo-2,5-dipropyloxybenzene, and 2,5-diethynyl-1,4-dipropoxybenzene[22] were prepared according to their respective literature procedures.



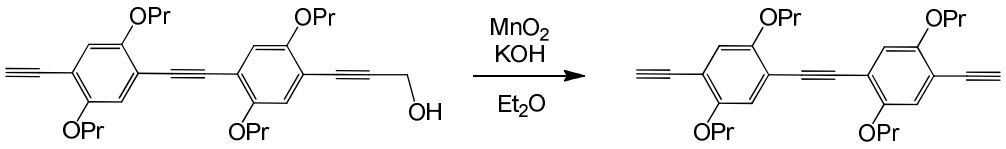
8-Iodo-1-(4-(2,5-dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-naphthalene, III-1. A solution of **II-5** (900 mg, 1.94 mmol), 1,8-diiodonaphthalene (2.00 g, 5.26 mmol), $Pd(Ph_3P)_2Cl_2$ (13.6 mg, 19.4 μmol) and CuI (7.40 mg, 38.8 μmol) in 20 mL 1:1 THF and piperidine under Ar was stirred at 70 ºC for 12 h. Et_2O (100 mL) was added and the mixture was washed with sat. NH_4Cl (100 mL), and H_2O (100 mL). The solvent was removed under reduced pressure and the residue subjected to column chromatography (1:9 v/v ethyl acetate:hexanes) to give the title compound as a dark brown viscous oil (585 mg, 44%). ^{1}HNMR ($CDCl_3$): δ 1.04 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.07-1.14 (m, 9 H, CH_3), 1.74-1.96 (m, 8 H, CH_2), 3.89 (t, ^3J = 6 Hz, 2 H, OCH_2), 4.00 (t, ^3J = 6 Hz, 2 H, OCH_2), 4.02 (t, ^3J = 6 Hz, 2 H, OCH_2), 4.04 (t, ^3J = 6 Hz, 2 H, OCH_2), 6.83-6.844 (m, 2 H, Ar-H), 7.06-7.07 (m, 2H, Ar-H), 7.10 (dd, 1H, ^3J = 7 Hz, ^3J = 8 Hz, naphthyl-H), 7.21 (s, 1 H, Ar-H), 7.44 (dd, ^3J = 7 Hz, ^3J = 8 Hz, 1 H, naphthyl-H), 7.79 (dd, ^4J = 1 Hz, ^3J = 8 Hz, 1H, naphthyl-H), 7.83 (dd, ^4J = 1 Hz, ^3J = 8 Hz, 1 H, napthyl-H), 7.94 (dd, ^4J = 1 Hz, ^3J = 8 Hz, 1 H, naphthyl-H), 8.29 (dd, ^4J = 1 Hz, ^3J = 7 Hz, 1 H, naphthyl-H). ^{13}CNMR ($CDCl_3$): δ 10.5 (CH_3), 22.7 (CH_2), 70.1 (OCH_2), 71.2 (CH_2), 71.3 (CH_2), 89.9 (≡C), 91.5 (≡C), 93.0 (≡C), 94.2 (≡C), 98.1, 114.2, 116.2, 116.6, 117.2,

118.5, 123.1, 125.5, 127.0, 130.0, 130.3, 131.7, 134.8, 136.1, 142.5, 152.7 (CO-Ar), 153.4 (CO-Ar), 153.5 (CO-Ar), 153.9 (CO-Ar). MS (MALDI): m/z (%) 686.2; HRMS found 686.19195, Δ = 1.9 ppm for $C_{38}H_{39}O_4I$.



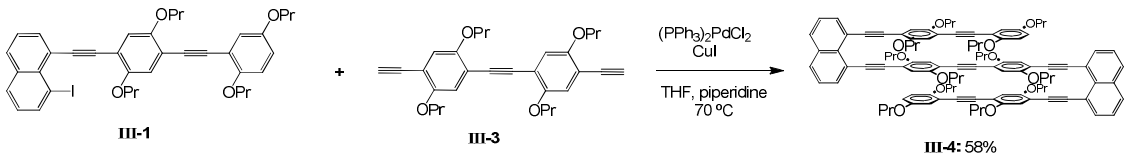
1-(4-(4-Ethynyl-2,5-dipropyloxyphenylethynyl)-2,5-dipropyloxyphenyl)propyn-3-ol, III-2. A solution of 2,5-diethynyl-1,4-dipropyloxybenzene (1.93 g, 8.00 mmol), **II-3** (1.50 g, 4.00 mmol), $Pd(Ph_3P)_2Cl_2$ (28.0 mg, 4.00 μmol) and CuI (15.2 mg, 8.00 μmol) in 40 mL THF and piperidine under Ar was stirred for 12 h. The mixture was extracted with Et_2O (150 mL), and the organic layer was washed with sat. aq. NH_4Cl (150 mL), and H_2O (150 mL). The organic layer was separated and concentrated under reduced pressure and the residue was subjected to column chromatography (25:75 ethyl acetate:hexanes) to afford the title compound as a pale green solid (1.32 g, 67% yield). m.p. = 59-62 ºC. ^{1}HNMR ($CDCl_3$): δ 1.00-1.07 (m, 12 H, CH_3), 1.75-1.88 (m, 8 H, CH_2), 2.16 (t, ^3J = 6 Hz, 1 H, OH), 3.36 (s, 1 H, ≡CH), 3.33 (s, 1 H, ≡C-H) 3.92-3.98 (m, 8 H, OCH_2), 4.51 (s, 1 H, CH_2-OH), 4.53 (s, 1 H, CH_2-OH), 6.92 (s, 1 H, Ar-H), 6.96 (s, 1 H, Ar-H), 6.98 (s, 2 H, Ar-H) . ^{13}CNMR ($CDCl_3$): δ 10.4 (CH_3), 10.5 (CH_3), 22.4 (CH_2), 22.5 (CH_2), 51.7 (CH_2OH), 70.9 (OCH_2), 71.0 (OCH_2), 71.1 (OCH_2), 79.9 (≡C), 81.9 (≡C), 82.3 (≡C), 91.1 (≡C), 91.2 (≡C), 92.6 (≡C), 112.5 (Ar), 113.2 (Ar), 114.3 (Ar), 114.7 (Ar), 117.0 (CH-Ar), 117.1 (CH-Ar), 117.4 (CH-Ar), 117.9 (CH-Ar), 153.1 (CO-Ar), 153.3 (CO-Ar), 153.4 (CO-Ar), 154.0 (CO-Ar). IR (AT-IR, neat): 3395, 3272, 2960, 2930, 2868, 1602,

1499, 1383, 1197, 1011, 858 cm^{-1}. MS (EI): m/z (%) 488.2 (100), 43.2 (8)[C_3H_7]; HRMS found 488.25763, Δ = 2.8 ppm for $C_{31}H_{36}O_5$.



II-2 **III-3:** 55%

1,2-(2,5-Dipropyloxyphenylacetylene)ethylene, III-3. MnO_2 (1.06 g, 12.3 mmol) and KOH (0.679 g, 12.3 mmol) was added in four portions to a solution of **III-2** (0.603 mg, 1.23 mmol) in Et_2O (100 mL). The mixture was filtered and the solvent was removed under reduced pressure to afford the title compound as a green solid (311 mg, 55%). m.p. = 73-78 ºC. ^{1}HNMR ($CDCl_3$): δ 1.03-1.10 (m, 12 H, CH_3), 1.78-1.90 (m, 8 H, CH_2), 3.35 (s, 2 H, ≡C-H), 3.94-4.00 (m, 8 H, OCH_2), 6.97 (s, 2 H, Ar-H), 6.99 (s, 2 H, Ar-H). ^{13}CNMR ($CDCl_3$): δ 10.4 (CH_3), 10.5 (CH_3), 22.5 (CH_2), 22.6 (CH_2), 70.9 (OCH_2), 71.0 (OCH_2), 79.9 (≡C), 82.3 (≡C), 91.2 (≡C), 112.6 (Ar), 114.7 (Ar), 117.0 (CH-Ar), 117.8 (CH-Ar), 153.2 (CO-Ar), 154.0 (CO-Ar). IR (AT-IR, neat): 3281, 2957, 2928, 2871, 2100, 1504, 1414, 1385, 1209, 985, 861 cm^{-1}. MS (MALDI): m/z (%) 458.2 (100)[M^+], 429.2 (25, 290 (15), 43.2 (10)[C_3H_7]. HRMS found 458.24813, Δ = 5.3 ppm for $C_{30}H_{34}O_4$.



8-Dinaphthyl-(4-(2,5-dipropyloxyphenylethynyl)-2,5-(dipropyloxyphenylethynyl)-1-((2,5-dipropyloxyphenylethynyl)ethylene), III-4. A solution of **III-1** (585 mg, 0.852 mmol), **III-3** (130 mg, 0.284 mmol), $Pd(Ph_3P)_2Cl_2$ (6.0 mg, 8.5 μmol) and CuI (3.0 mg, 21 μmol) in 8 ml of 1:1 THF and piperidine under Ar was stirred at 70ºC for 12 h. The mixture was extracted with Et_2O (100 mL) and the organic layer washed with sat. aq. NH_4Cl (100 mL) and H_2O (100 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (15:85 v/v ethyl acetate:hexanes) to afford the title compound as an iridescent green compound (260 mg, 58% yield). m.p. = 160-164 ºC. ^{1}HNMR ($CDCl_3$): δ 0.95-1.13 (m, 36 H, CH_3), 1.66-1.92 (m, 24 H, CH_2), 3.41 (t, ^3J = 6 Hz, 4 H, OCH_2), 3.45 (t, ^3J = 6 Hz, 4 H, OCH_2), 3.83 (t, ^3J = 6 Hz, 4 H, OCH_2), 3.89-3.98 (m, 12 H, OCH_2), 6.80-6.81 (m, 4 H, Ar-H), 6.82 (s, 2 H, Ar-H), 6.86 (s, 2 H, Ar-H), 6.96 (s, 2 H, Ar-H), 6.98 (s, 2 H, Ar-H), 7.00-7.02 (m, 2 H, Ar-H), 7.48 (dd, ^3J = 8 Hz, ^3J = 8 Hz, 4 H, naphthyl-H3, 6), 7.83 (d, ^3J = 8 Hz, 4 H, naphthyl-H), 7.90 (d, ^3J = 8 Hz, 4 H, naphthyl-H). ^{13}CNMR ($CDCl_3$): δ 10.4 (CH_3), 10.6 (CH_3), 22.5 (CH_2), 22.6 (CH_2), 70.0 (OCH_2), 70.2 (OCH_2), 70.3 (OCH_2), 70.7 (OCH_2), 70.9 (OCH_2), 71.3 (OCH_2), 89.9 (≡C), 91.4 (≡C), 91.6 (≡C), 93.7 (≡C), 93.8 (≡C), 95.6 (≡C), 95.7 (≡C), 114.3, 116.5, 116.6, 118.5, 121.1, 121.2, 125.6, 129.4, 130.9, 134.0, 135.0, 152.7 (CO-Ar), 153.3 (CO-Ar), 153.4 (CO-Ar), 153.5 (CO-Ar), 153.8 (CO-Ar). MS (MALDI): m/z (%) 1575.7 (100)[M+]. HRMS found 1574.7962, Δ = 10 ppm for $C_{106}H_{110}O_{12}$. Elem. Anal. calcd. C 80.78, H 7.04, O 12.18; found C 80.83, H 7.11, O 12.28.

3.3. Results And Discussion

3.3.1. Synthesis of Oligo(PE) Triad Components

Our previous studies of naphthalene-bridged dialkoxy phenylene ethynylene oligomers has provided us with synthetic routes for the building blocks of the oligo PE triad prepared in this study as shown in Figure 3.2.

Synthesis of the naphthalene-bridged oligo PE triad was accomplished through a convergent synthesis where two mono-iodo naphthalene components bearing the exterior conjugated arms were coupled to a dialkyne; which comprises the central conjugated tier. For the synthesis of the external units, alkyne dimer **II-5** was exposed to an excess of 1,8-diiodonaphthalene to afford the mono-iodo exterior arm component **III-1** in 44% yield. The core dialkyne **III-3** was prepared by treatment of the bifunctional iodo-alcohol **II-3** with an excess of 2,5-diethynyl-1,4-dipropyloxybenzene to give a PE dimer **III-2** with a terminal acetylene on one end and a propargyl alcohol on the other end. This alcohol was subsequently deprotected to afford the dialkyne **III-3** in 55% yield. Reaction of the two components **III-1** and **III-3** in a 2:1 molar ratio afforded the triad **III-4** in 58% yield.

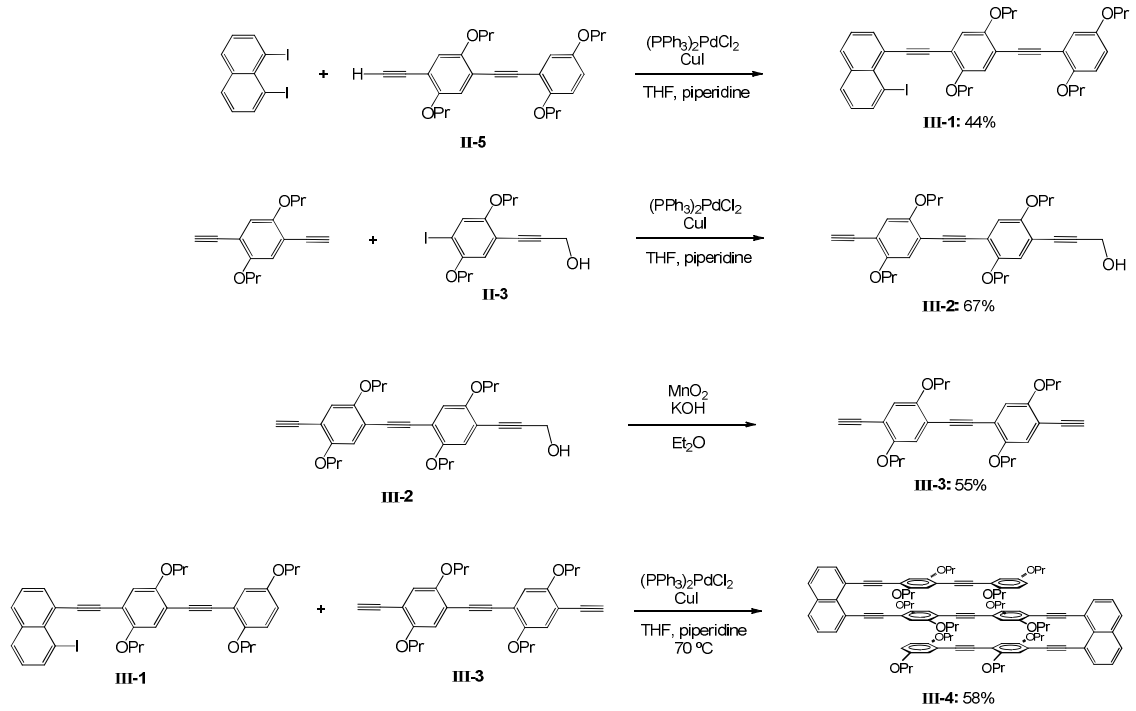


Figure 3.2. Synthesis of the oligo PE triad, **II-4**.

3.3.2. Structural Characterization: ^{1}H NMR and ^{13}C NMR Spectroscopy

All compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. One of the key components, mono-iodide **III-1** was identified by the splitting pattern of the protons of the unsymmetrically substituted naphthalene by a comparison to the spectra of stacked dimer **II-9** and the starting material 1,8-diiodonaphthalene. The assignment shown in Figure 3.3 is consistent with the unsymmetrically-substituted naphthalene bearing one iodide and one PE dimer arm.

The full [1]HNMR spectrum of oligo PE triad **III-4** is given in Figure 3.4. The spectrum shows signals from protons of the 12 sets of propyloxy side chains along the phenylene ethynylene units. The protons of the 1,8-substituted naphthalene show an identical splitting pattern to protons with other 1,8-di-(oligo PE)-substituted naphthalenes such as **II-9**.

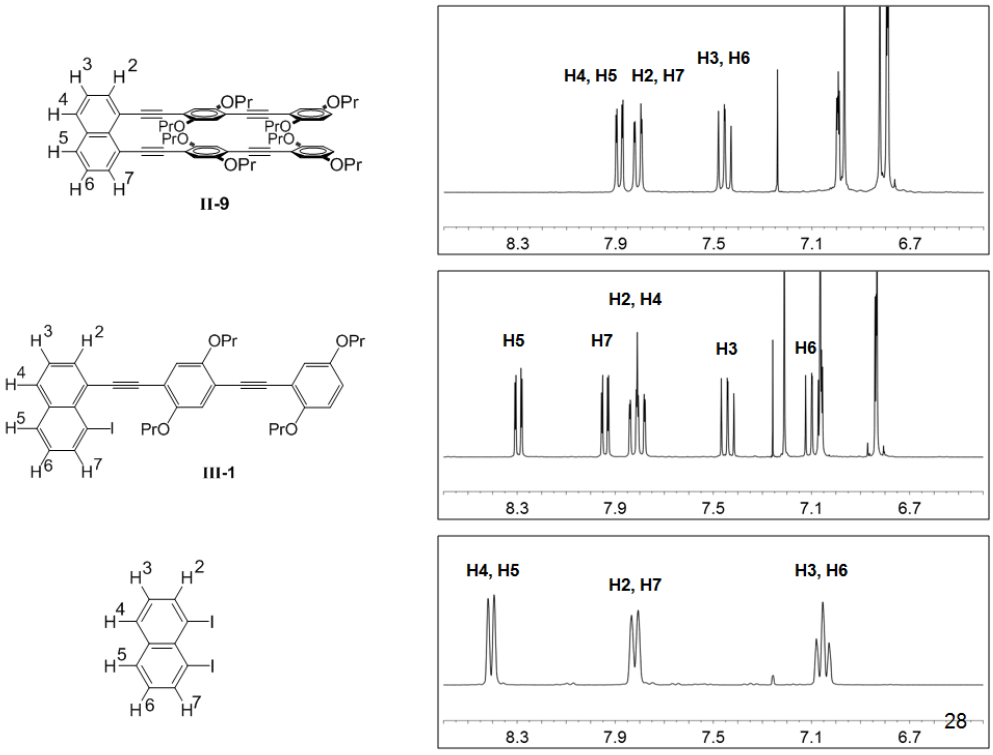


Figure 3.3. [1]H NMR spectroscopy comparison of the aromatic regions of two tier naphthalene-bridged dimer **II-9**, triad **III-1**, and 1,8-diiodonaphthalene.

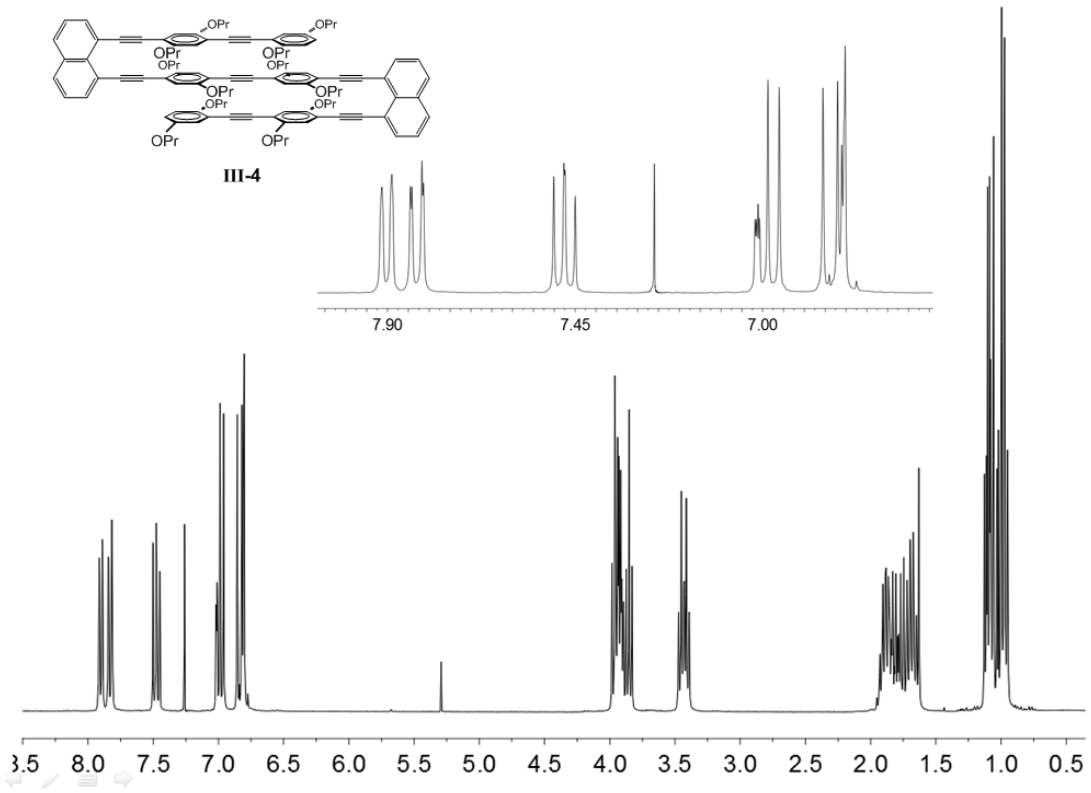


Figure 3.4. Full [1]HNMR spectrum of **III-4** with expansion of aromatic region.

3.3.3. X-ray Structural Analysis

Upon purification of **III-4**, we observed the formation of small, fine crystals and attempted to grow crystals suitable for X-ray crystal structure analysis. This afforded the molecular structure shown in Figures 3.5 and the crystal packing structure shown in Figure 3.6-7. Deformations associated with the naphthalene moiety in **III-4** can be seen which is consistent with the naphthyl-bridged dipropyloxy oligo(PE)s reported in Chapter 2. In Figure 3.5 A, the C14-C18-C33 angle is 136º; which is slightly less than the same angle for naphthyl-bridged monomer **II-8** measured at 142º. In Figure 3.5B, the first set of phenylenes that are adjacent to the naphthalene of **III-4** are 5.9 Å apart measured from the C16-C31 distance which is closer than the C18-C30 distance of 6.7 Å measured for **II-8**.

Figure 3.6 illustrates the interaction of two molecules of **III-4** in the C2 packing structure. The C32-C32 distance between two molecules shows the phenylenes are 4.0 Å apart and are oriented head-to-head with one another, which is atypical for oligo(PE)s. This suggests that dispersion of the oxygen atoms or alkoxy substitutents could be playing a primary role in the ordering of this crystal structure. Figure 3.7 shows the complete crystal structure of **III-4**; although two of the central tiered oligo(PE)s appear to be aligned to one another 13 Å apart, there are no intermolecular π-stacking interactions within the packing structure.

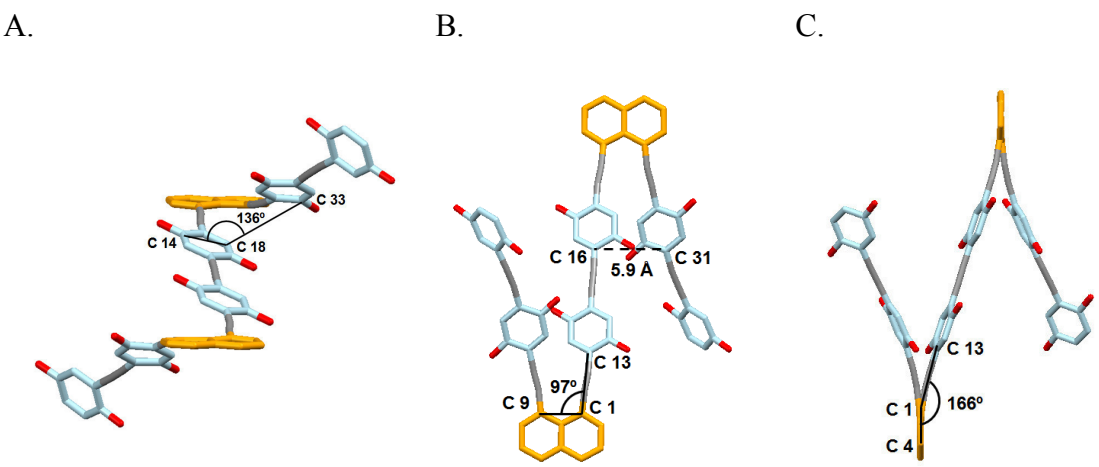


Figure 3.5. X-ray crystal measurements of the molecular structure of oligo (PE) triad **III-4**. Note that propyl chains have been omitted for clarity.

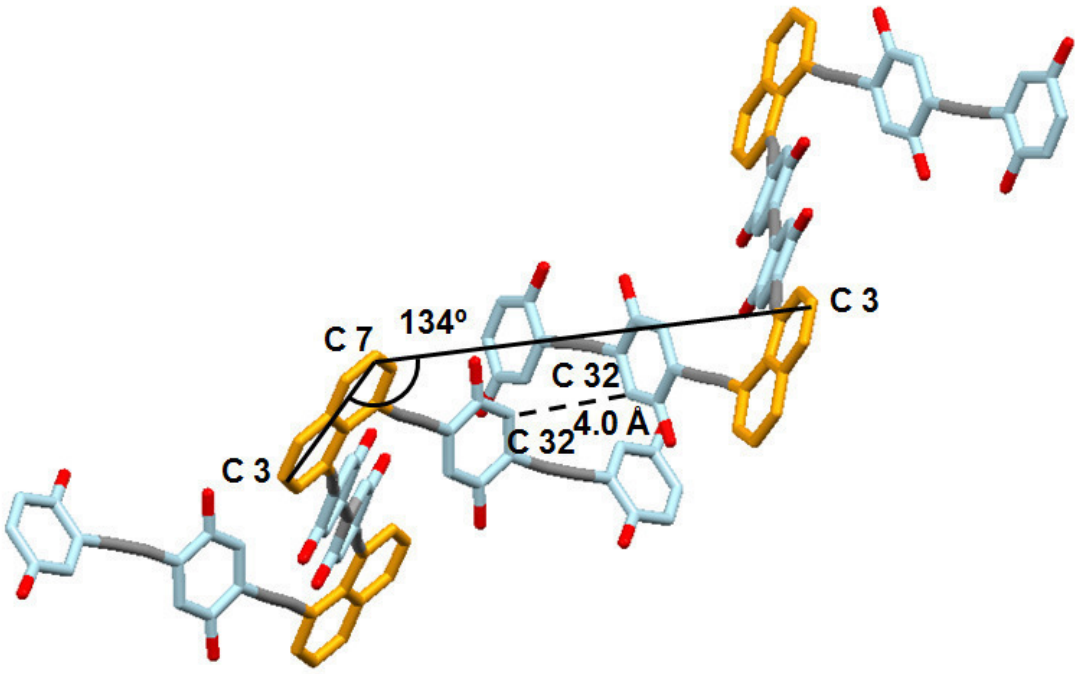


Figure 3.6. X-ray crystal structure in the packing of two molecules of oligo(PE) triad **III-4**. The propyl chains have been omitted for clarity.

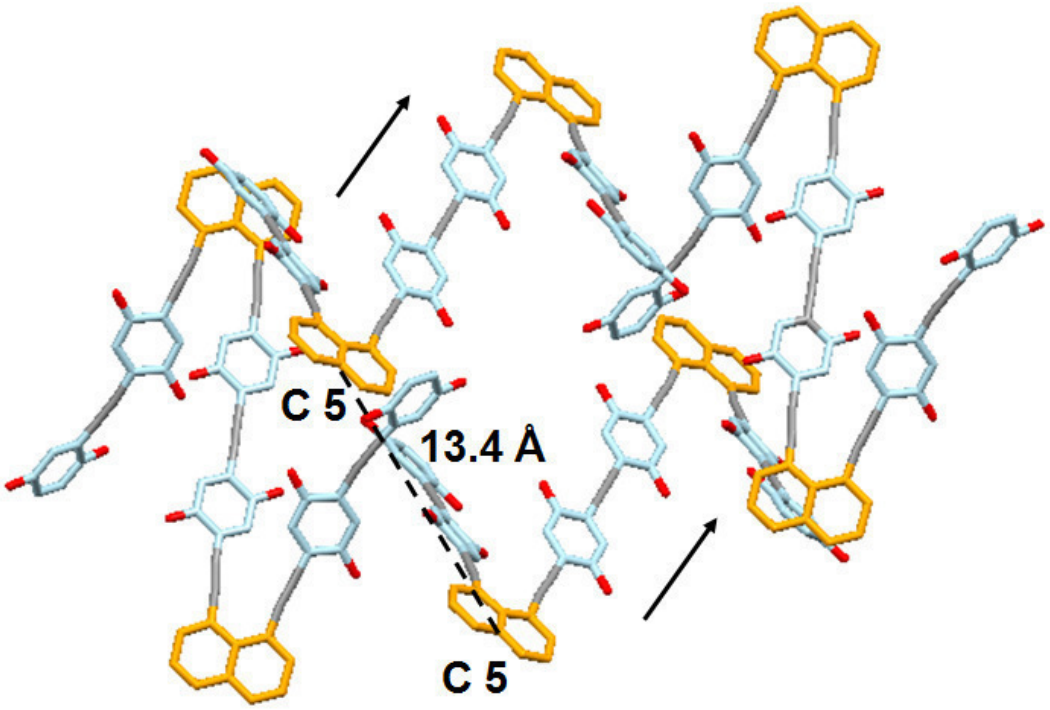


Figure 3.7. X-ray crystal C2 packing structure of oligo (PE) triad **III-4**. Note the arrows show the alignment of two planarized PE oligomers amongst two molecules in the packing structure. Propyl chains have been omitted for clarity.

3.3.4. Electrochemistry of Oligo(PE) Triad

The electrochemical properties of **III-4** were measured by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), Tables 3.1 and 3.2, and Figure 3.8. Analysis of this compound indicated a small pre-peak at 1.42 V followed by a two-wave oxidations at 1.59 and 1.83 V. These oxidations were non-reversible which can be due to electropolymerization of the analyte.[2] The presence of the pre-peak could be due to several factors including conformational variations,[20] or formation of a meta-stable charged species.

Table 3.1. Electrochemical CV data for **III-4** and comparison to compounds reported in Chapter 2.

	Potential / V			
Compound	I_{ox}	II_{ox}	I_{red}	II_{red}
II-8	1.77	1.96	1.58	1.38
II-9	1.63	1.76	1.63	1.32
II-7	1.71	-	-	-
II-10	1.56	1.70	1.58	1.33
III-4	1.59	1.83	1.42	-

Table 3.2. Electrochemical DPV data for **III-4** and comparison to compounds reported in Chapter 2.

	Potential / V	
Compound	I_{ox}	II_{ox}
II-8	1.74	1.92
II-9	1.63	1.77
II-7	1.71	-
II-10	1.57	1.70
III-4	1.58	1.81

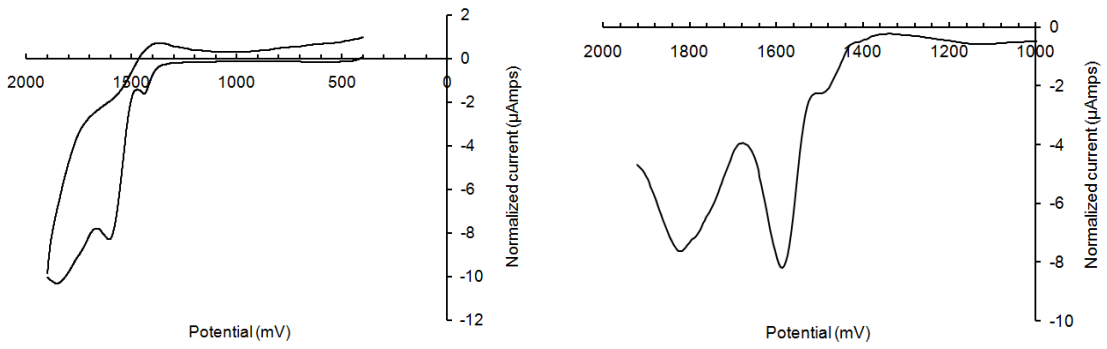


Figure 3.8. CV (left) and DPV (right) of compound **III-4**. Measurements were taken at 100 mV/sec with gold electrode in 0.1 M NBu_4PF_6 with dichloromethane. Analyte concentration is ~10 µM.

A comparison of previously reported naphthyl-bridged oligo PEs (Table 3.1 and Figure 3.9) found that the first oxidation wave potential of **III-4** was slightly lower than for the corresponding naphthyl-bridged dimer, **II-9**. However, it seems that the second oxidation wave potential is slightly higher. This would suggest that formation of the first cation is stabilized by an increase in the energy of the HOMO for the triad but subsequent formation of the di-cation is less-favored.

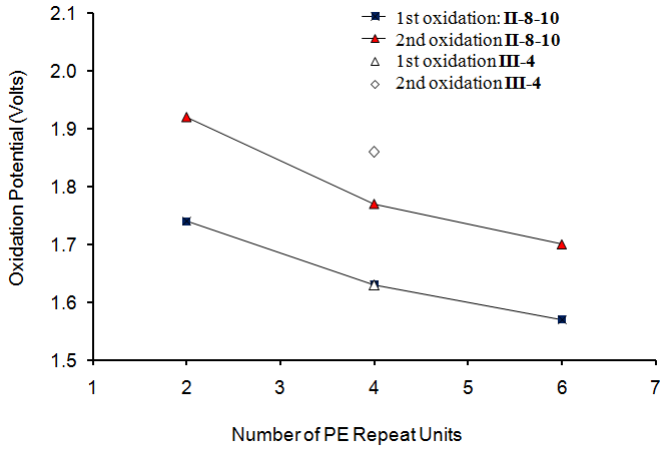


Figure 3.9. Plot comparing oxidations potentials measured by DPV for compounds **II-7-10** to **III-4**.

3.3.5. UV-Vis And Fluorescence Measurements Of Oligo(PE) Triad and Comparison To Single Naphthalene-Bridged and Unbridged Oligo (PE)s

Our previous results on naphthyl-bridged dimer, **II-9** presents the opportunity for a comparison of the spectroscopic properties to the triad compound **III-4**. This should be able to identify the effect of integrating naphthalene units amongst the oligomers has on the spectroscopic properties of PE oligomers. A side-by-side comparison of the alkyne oligomer **II-5** and single-naphthalene-bridged oligomer **II-9**, each containing components that make up **III-4**, is given in Table 3.3 and Figure 3.10, along with the measured properties of **III-4**.

The UV-vis spectrum of **III-4** (λ_{max}= 385 nm) is very similar in features to **II-9** (λ_{max}= 384 nm), both are red-shifted relative to **II-5** (λ_{max}= 341 nm). The fluorescence emission of **III-4** has the same λ_{max} as **II-9** at 455 nm where both have a Stokes shift approximately 70 nm. The spectrum of **III-4** is much sharper than **II-9** and has a shoulder at longer wavelength. The sharp profile of the fluorescence spectrum of **III-4** could be due to a chromophore unit that consists mainly of the central oligomer tier that is planarized and extends through the conjugation of the two naphthalene bridging units.

Table 3.3. UV-vis absorbance and fluorescence data for **II-5**, **II-9**, and **III-4**.

Compound	Number of consecutive phenylene ethynylene rings	$\lambda_{abs\ solution}$ (nm)	Molar absorptivity $\varepsilon /\times 10^3$	$\lambda_{em\ solution}$ (nm)	Stokes shift $\lambda_{abs\ solution}$ (nm) - $\lambda_{em\ solution}$ (nm)
II-5	2	341	25.8	394	53
II-9	2	384	79.7	455	71
III-4	2	385	202.2	455	70

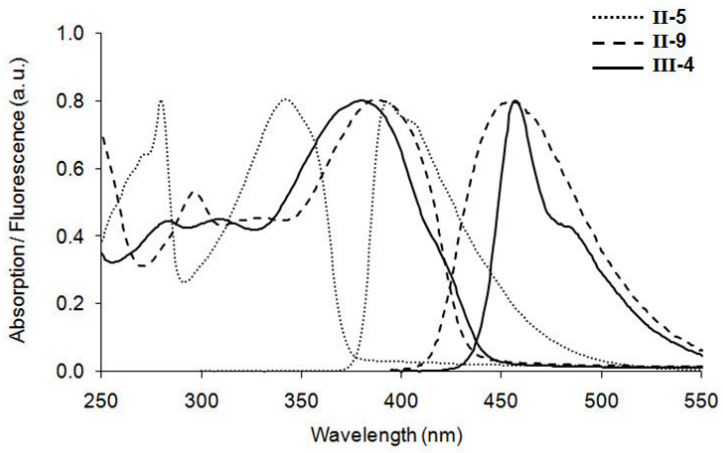


Figure 3.10. Normalized UV-vis absorption and fluorescence spectrum of **II-5** (dotted), **II-9** (dashed), and **III-4** (solid) in CH_2Cl_2 (~10^{-6} M).

3.4. Conclusion

We have reported the synthesis, structural, electrochemical, and spectroscopic properties of **III-4**, which constitutes a three-tiered oligo(PE) triad. Chemical structure was defined by NMR and X-ray crystal structures. Electrochemical measurements show one-electron oxidation that is lower than the naphthyl-bridged dimer, **II-9**. Spectroscopic measurements show that the triad **III-4** and naphthyl-bridged dimer **II-9** have excitation and emission spectra at similar at similar λ_{max} values; however, the emission spectrum of **III-4** is very sharp and well-defined- narrower than that of **II-9**. We believe these observations to be characteristic of a chromophore segment from the central PE oligomer that is planarized and extends into the naphthalene bridging unit.

3.5. References

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CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF NAPHTHYL-BRIDGED OLIGO(PHENYL ETHYNYLENE)S WITH A SINGLE ALKOXY CHAIN AT THE TERMINUS

4.1. Introduction

Advances in the field of organic chemistry have brought about new conjugated polymer structures for application in devices such as thin-film transistors,[1-3] photovoltaic solar cells,[4-6] and light-emitting diodes.[7-8] However, with the development of new structures comes a need to understand structure-property relationships. A fundamental feature of conjugated polymers with aromatic subunits is how intermolecular π-stacking interactions influence these properties.[9] These interactions are present between segments of polymers in which the aromatic units stack in a co-facial manner, and play a role in the mobility of charge carriers in conjugated materials. Understanding and attaining control over π-stacking interactions will be critical to the development of conjugated polymers with enhanced properties for deployment in electronic devices.

One approach to exploring π-stacking interactions between conjugated polymer chains is synthesis of models which use a covalent bridge to hold two aromatic units in close proximity. An example of such a scaffold is the bis(areno)bicycloundecanone core developed by Mataka[10-12] and modified by Collard[13] to hold thiophene oligomers in a cofacial arrangement. These oligomers were oxidized with $FeCl_3$ to provide the dication. The ESR spectrum of the dication indicated that it was spinless, and new absorbance

bands in the UV-vis/near IR are consistent with a π-dimer; a lower-energy spin-paired electronic state brought about by close contact of the π-faces resulting in an interaction of the π-orbitals. These π-dimers have been suggested as models for bipolaron-like charge carriers in p-doped conjugated polymers.

Our exploration of π-stacking makes use of stacked oligo(1,4-phenylene ethynylene)s, oligo(PE)s. The oligomers have a rigid-rod structure, and they may be prepared using a variety of well-established arene-alkyne coupling methods.[14] We have already shown that substitution of oligo(dialkoxy-PE)s on the 1 and 8-positions of naphthalene imposes a highly twisted and splayed structure with little π-stacking (Chapter 3). These distortions could originate from: (i) the strong dipoles associated with oxygen atoms; or (ii) the electron-donating character of the alkoxy substituents increasing the electron density of the aromatic rings, leading to electrostatic repulsion. To minimize these effects we prepared oligo(1,4-phenylene ethynylene)s with a single alkoxy terminus that were coupled to a 1,8-naphthalene bridge.

4.2. Experimental

4.2.1. General Procedures

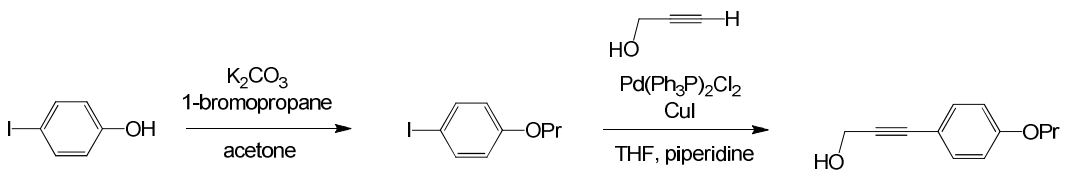
All reactions were conducted with distilled solvents in oven-dried and argon-charged glassware. All reagents were used as received from commercial suppliers without prior purification. Analytical thin layer chromatography (TLC) was performed on precoated aluminum-backed plates purchased from Sorbent Technologies (silica gel 60 F254; 0.25 mm thickness). Flash column chromatography was performed on silica gel 60 (230-400 mesh ASTM) from Sorbent Technologies. ^{1}H and ^{13}C NMR spectra were

recorded on a Varian Gemini spectrometer (300 MHz for ^{1}H, 100 MHz for ^{13}C). NMR spectra were measured in solutions of deuterated chloroform ($CDCl_3$) with tetramethylsilane as the internal standard, and reported in parts per million (ppm). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet.

IR spectra were collected on a Nicolet 4700 FTIR with an ATR attachment from SmartOrbit Thermoelectronic Corp with samples as neat films. Mass spectra, including high resolution spectra, were measured using EI on a Waters 70SE instrument or MALDI Micromass TofSpec2E instrument. Elemental analyses were obtained from Atlantic Microlabs in Norcross, Georgia. UV-vis/near-IR was recorded on a Perkin-Elmer Lamda 19 spectrometer. Fluorescence measurements were made on a Shimadzu RF-5301 PC in solutions in dichloromethane at ~10^{-6} M. X-ray Crystal structures were collected on a Bruker Apex-II CCD by Kenneth Hardcastle at Emory University X-ray facility.

4.2.2. Synthetic Procedures

1,4-Diiodobenzene was obtained from Alfa Aesar and 1,4-diethynyl-benzene was prepared according to a literature procedure.[15]

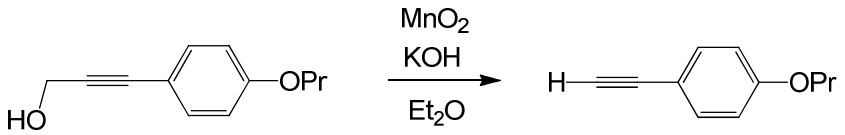


IV-1a: quant. **IV-1b:** 58%

1-(4-Propyloxyphenyl)propyn-3-ol, IV-1b. A solution of 4-iodophenol (10.0 g, 45.4 mmol) and K_2CO_3 (62.8 g, 454 mmol) in acetone (250 mL) was heated to reflux under Ar. 1-Bromopropane (20 mL, 0.22 mmol) was added dropwise and the reaction mixture was heated for 12 h. The mixture was extracted with diethyl ether (250 mL) and the organic layer was washed with DI H_2O (2 × 250 mL). The solvent was removed under reduced pressure. Excess water was removed by re-dissolving the mixture in CH_2Cl_2 separating the aqueous phase and drying over $MgSO_4$. The solvent was again removed to afford *4-propyloxy-iodobenzene*, **IV-1a** (11.2g, quant.) which was used without further purification. ^{1}H NMR ($CDCl_3$): δ 1.04 (t, J = 7 Hz, 3 H, CH_3), 1.74-1.86 (m, 2 H, CH_2), 3.87 (t, J = 7 Hz, 2 H, OCH_2), 6.68 (d, J = 9 Hz, 2 H, Ar-H), 7.55 (d, J = 9 Hz, 2 H, Ar-H). ^{13}CNMR ($CDCl_3$): δ 10.5, 22.4, 69.5, 82.4, 116.9, 138.1, 158.9. IR (AT-IR, neat): 2957, 2930, 2874, 1585, 1485, 1280, 1240, 1177, 974, 815, 619, 499. MS (EI): m/z (%) 262 (40) [M+], 188.1 (35), 146 (77). HRMS calculated for $C_9H_{11}IO$, 261.98547; found 261.98746, Δ = 7.6 ppm.

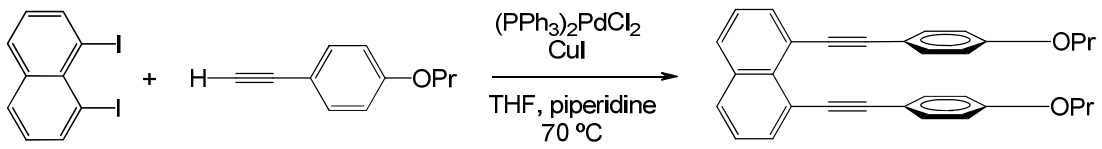
A mixture of crude 4-propyloxy-iodobenzene, propargyl alcohol (3.82 g, 68.1 mmol), $Pd(Ph_3P)Cl_2$ (318 mg, 0.454 mol) and CuI (172 mg, 0.908 mol) in 454 mL of a 1:1 v/v mixture of THF and piperidine was stirred for 12h under Ar. The mixture was extracted with Et_2O (200 mL). The extract was washed with sat. aq. NH_4Cl (200 mL) and

DI H_2O (200 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (25% v/v ethyl acetate: hexanes) to afford the title compound as a colorless crystalline solid (5.00 g, 58% yield). m.p = 70-72 ºC. ^{1}H NMR ($CDCl_3$): δ 1.03 (t, ^3J = 7 Hz, 3 H, CH_3), 1.67 (t, J = 6 Hz, 1 H, OH), 1.72-1.86 (m, 2 H, CH_2), 3.91 (t, ^3J = 7 Hz, 2 H, OCH_2), 4.47 (s, 1 H, ≡C-CH_2), 4.49 (s, 1 H, ≡C-CH_2), 6.82 (d, J = 9 Hz, 2 H, Ar-H), 7.36 (d, J = 9 Hz, 2 H, Ar-H). ^{13}CNMR ($CDCl_3$): δ = 10.4 (CH_3), 22.4 (CH_2), 51.7 (CH_2-OH), 69.5 (OCH_2), 85.7 (≡C), 85.7 (≡C), 114.2 (Ar), 114.4 (Ar), 133.1 (Ar). IR (AT-IR, neat): 3282, 2967, 2933, 2238, 1602, 1509, 1253, 1014, 838 cm^{-1}. MS (EI): m/z (%) 190.2 (100) [M^+], 147.1 (50) [M^+-C_3H_7], 91.1 (15), 42.9 (5). HRMS calculated for $C_{12}H_{14}O_2$, 190.09938; found 190.09973, Δ = 1.9 ppm.



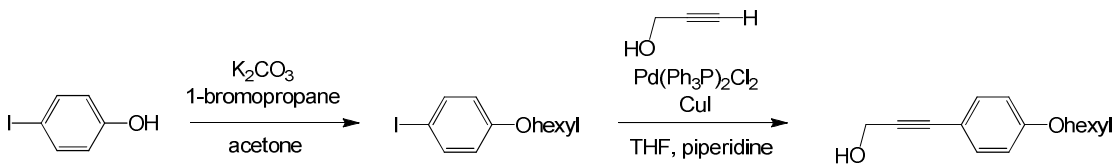
IV-1b **IV-2:** 76%

(4-Propyloxyphenyl)acetylene, IV-2. MnO_2 (22.8 g, 262 mmol) and potassium hydroxide (14.7 g, 262 mmol) were added in four separate portions to **IV-1b** (5.00 g, 26.2 mmol) in Et_2O (100 mL) and the mixture was stirred at room temperature. The progress of the reaction was monitored by TLC until no starting material was observed. The mixture was diluted with Et_2O (300 mL) and the solution was filtered through a plug of silica in a fritted funnel. The solvent was removed under reduced pressure to afford the title compound as a colorless oil (3.20 g, 76%). ^{1}H NMR ($CDCl_3$): δ 1.04 (t, ^3J = 7 Hz, 3 H, CH_3), 1.75-1.86 (m, 2 H, CH_2), 3.00 (s, 1 H, ≡C-H), 3.92 (t, ^3J = 7 Hz, 2 H, OCH_2), 6.84 (d, J = 9 Hz, 2 H, Ar-H) 7.42 (d, J = 9 Hz, 2 H, Ar-H). ^{13}CNMR ($CDCl_3$): δ = 10.4 (CH_3), 22.5 (CH_2), 69.5 (OCH_2), 75.6 (≡C), 83.7 (≡C), 113.8 (Ar-H), 114.4 (Ar-H), 133.5 (Ar-H), 159.5 (Ar-H). IR (AT-IR, neat): 3285, 2960, 2933, 2877, 2103, 1605, 1502, 1240, 977, 831, 534 cm^{-1}. MS (EI): m/z (%) 160.1 (25) [M^+], 118 (100), 42.9 (35). HRMS calculated for $C_{11}H_{12}O$, 160.08882; found 160.08850, Δ = 1.9 ppm.



IV-2 **IV-3:** 47%

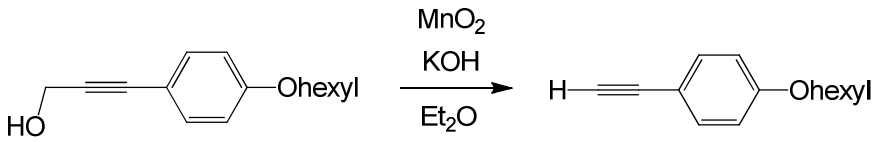
1,8-(4-Propyloxyphenylethynyl)naphthalene, IV-3. A solution of 1,8-diiodonaphthalene (0.260 g, 0.664 mmol), **IV-2** (0.548 g, 3.42 mmol), $Pd(Ph_3P)Cl_2$ (48 mg, 68 μmol) and CuI (130 mg, 68.3 μmol) in 13 mL of a 1:1 v/v mixture of THF and piperidine was heated to 70 ºC under Ar and stirred for 12 h. The mixture was extracted into Et_2O (30 mL) and washed with sat. aq. NH_4Cl (100 mL) and DI H_2O (100 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (10:90 v/v ethyl acetate/hexanes) to afford the title compound as a beige solid (140 mg, 47% yield). m.p. = 116-119 ºC. ^{1}H NMR ($CDCl_3$): δ 1.04 (t, ^3J = 7 Hz, 6 H, CH_3), 1.74-1.86 (m, 4 H, CH_2), 3.86 (t, ^3J = 7 Hz, 4 H, OCH_2), 6.67 (d, J = 9 Hz, 4 H, Ar-H), 7.30 (d, J = 9 Hz, 4 H, Ar-H), 7.44 (dd, J = 8 Hz, 2 H, naphthyl H 3, 6), 7.80 (d, J = 8 Hz, 2 H, naphthyl-H), 7.85 (d, J = 8 Hz, 2 H, naphthyl-H). ^{13}CNMR ($CDCl_3$): δ 10.5 (CH_3), 22.5 (CH_2), 69.4 (OCH_2), 88.4 (≡C), 96.8 (≡C), 114.1, 115.8, 121.2, 125.5, 129.2, 131.4, 133.0, 134.1, 134.5, 158.8. IR (AT-IR, neat): 3050, 2963, 2933, 2870, 2200, 1605, 1562, 1509, 1246, 825 cm^{-1}. MS (EI): m/z (%) 444.1 (100) [M^+], 359.1 (10)[M^+ - 2 × C_3H_7], 331.1 (10). HRMS calculated for $C_{32}H_{28}O_2$, 444.20893; found 444.20716, Δ = 4.0 ppm.



1-(4-Hexyloxyphenyl)propyn-3-ol, IV-4b. This compound was made using the same procedure as **IV-1.** A solution of 4-iodophenol (10.0 g, 45.4 mmol), K_2CO_3 (62.8 g, 0.454 mol) in acetone (250 mL) was heated to reflux under Ar. 1-Bromohexane (30.0 g, 0.182 mol) was added dropwise and the reaction mixture was heated for 12 h. The mixture was extracted with diethyl ether (250 mL) and the organic layer was washed with DI H_2O (2 × 250 mL). The solvent was removed under reduced pressure. Excess water was removed by re-dissolving the mixture in CH_2Cl_2 and separating the aqueous phase and drying over $MgSO_4$. The solvent was removed to afford *4-hexyloxy-1-iodobenzene*, **IV-4a** (13.8 g, quant.) which was used without further purification. ^{1}H NMR ($CDCl_3$): δ 3.90 (t, J = 7 Hz, 2 H, OCH_2), 6.67 (d, J = 9 Hz, 2 H, Ar-H), 7.52 (d, J = 9 Hz, 2 H, Ar-H). MS (EI): m/z (%) 304 (100) [M+], 219.9 (90). HRMS calculated for $C_{12}H_{17}IO$, 304.03168; found 304.03168, Δ = 2.4 ppm.

A mixture of crude 4-hexyloxy-iodobenzene, propargyl alcohol (3.54 g, 63.1 mmol), $Pd(Ph_3P)Cl_2$ (295 mg, 0.421 mmol) and CuI (160 mg, 0.842 mmol) in 420 mL of a 1:1 v/v mixture of THF and piperidine was stirred for 12 h under Ar. The mixture was extracted with Et_2O (200 mL). The extract was washed with sat. aq. NH_4Cl (200 mL) and DI H_2O (200 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (25% v/v ethyl acetate:hexanes) to afford the title compound as a colorless crystalline solid (8.50 g, 86% yield for two steps). m.p. = 42-43

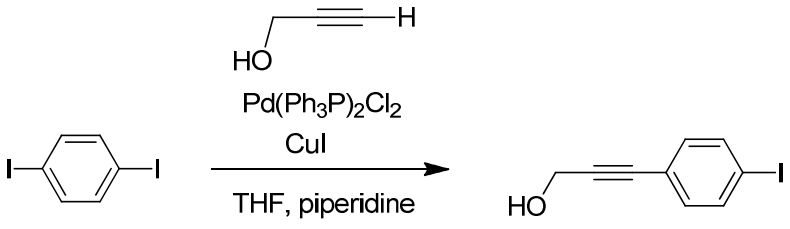
ºC. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, ^{3}J = 7 Hz, 3 H, CH_3), 1.27-1.45 (m, 6 H, alkyl-CH_2), 1.67-1.76 (m, 2 H, alkyl-CH_2), 3.84 (t, ^{3}J = 6 Hz, 2 H, OCH_2), 4.47 (s, 1 H, ≡C-CH_2), 4.48 (s, 1 H, ≡C-CH_2), 6.76 (d, J = 9 Hz, 2 H, Ar-H), 7.34 (d, J = 9 Hz, 2 H, Ar-H). ^{13}CNMR ($CDCl_3$): δ 13.7 (CH_3), 22.3 (CH_2), 25.4 (CH_2), 28.8 (CH_2), 31.3 (CH_2), 50.9 (CH_2), 67.7 (OCH_2), 85.1 (≡C), 85.8 (≡C), 114.1, 114.3, 132.9, 158.9. IR (AT-IR, neat): 3276, 2953, 2927, 2860, 2233, 1602, 1505, 1466, 1243, 1017, 835, 542 cm^{-1}. MS (EI): m/z (%) 232.1 (100) [M^+], 147.1 (75)[M^+-C_6H_{13}]. HRMS calculated for $C_{15}H_{20}O_2$, 232.14633; found 232.14629, Δ = 0.2 ppm.



IV-4b **IV-5:** 63%

(4-Hexyloxyphenyl)acetylene, IV-5. MnO_2 (30.3 g, 349 mmol) and potassium hydroxide (19.6 g, 349 mmol) were added in four separate portions to **IV-4b** (8.10 g, 34.9 mmol) in Et_2O (100 mL) at room temperature. The progress of the reaction was monitored by TLC until no more starting material was observed. The mixture was extracted with Et_2O (300 mL) and the solution was filtered through fritted funnel. The solvent was removed under reduced pressure to afford the title compound as a colorless oil (4.41 g, 63%). ^{1}H NMR ($CDCl_3$): δ 0.95 (t, ^{3}J = 7 Hz, 3 H, CH_3), 1.34-1.52 (m, 6 H, alkyl-CH_2), 1.74-1.84 (m, 2 H, alkyl-CH_2), 3.03 (s, 1 H, ≡C-H), 3.94 (t, ^{3}J = 7 Hz, 2 H, OCH_2), 6.85 (d, J = 9 Hz, 2 H, Ar-H), 7.44 (d, J = 9 Hz, 2 H, Ar-H). ^{13}CNMR ($CDCl_3$): δ

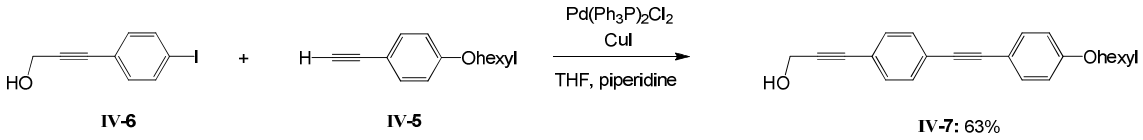
14.0 (CH_3), 22.5 (alkyl-CH_2), 25.6 (alkyl-CH_2), 29.1 (alkyl-CH_2), 31.5 (alkyl-CH_2), 67.9 (OCH_2), 75.6 (≡C), 83.7 (≡C), 113.8, 114.3, 133.4, 159.5. IR (AT-IR, neat): 3289, 2927, 2857, 2107, 1605, 1502, 1462, 1243, 1163, 831, 536 cm^{-1}. MS (EI): m/z (%) 202.2 (75) [M^+], 118 (100) [M^+-C_6H_{13}]. HRMS calculated for $C_{14}H_{18}O$, 202.13577; found 202.13381, Δ = 9.7 ppm.



IV-6: 64%

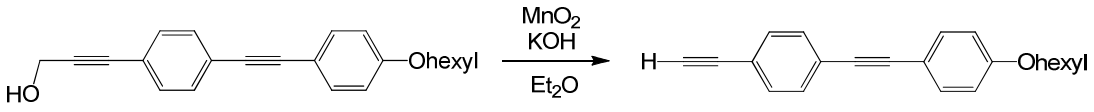
1-(4-Iodophenyl)propyn-3-ol, IV-6. A solution of 1,4-diiodobenzene (12.0 g, 36.4 mmol), $Pd(Ph_3P)Cl_2$ (127 mg, 0.182 mmol), CuI (69.0 mg, 0.362 mmol), and propargyl alcohol (1.02 g, 18.2 mmol) in 180 mL of a 1:1 v/v mixture of THF and piperidine was stirred for 12 h under Ar. The mixture was extracted with Et_2O (200 mL), and the extracts were washed with sat aq. NH_4Cl (200 mL), and DI H_2O (200 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (25:75 v/v ethyl acetate/hexanes) to afford the title compound as a yellow crystalline solid (3.02 g, 64% yield). m.p. = 99-101 ºC. ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 1 H, OH), 4.47 (s, 1 H, ≡C-CH_2), 4.48 (s, 1 H, ≡C-CH_2), 7.14 (d, *J* = 9 Hz, 2 H, Ar-H), 7.65 (d, *J* = 9 Hz, 2 H, Ar-H). ^{13}CNMR ($CDCl_3$): δ 51.6, 84.8, 88.6, 94.5, 122.0, 133.1, 137.4. IR (AT-IR, neat): 3319, 3229, 2917, 2857, 2236, 1575, 1482, 1031, 818,

526 cm^{-1}. MS (EI): m/z (%) 257.9 (100) [M^+], 103 (60), 77 (35). HRMS calculated for C_9H_7OI, 257.95417; found 257.95581, Δ = 6.4 ppm.



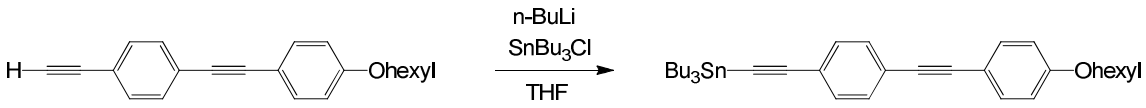
IV-6 **IV-5** **IV-7:** 63%

1-(4-(4-Hexyloxyphenylethynylene)phenyl)propyn-3-ol, IV-7. A solution of **IV-6** (1.97 g, 7.64 mmol), $Pd(Ph_3P)Cl_2$ (53.6 mg, 76.4 μmol), CuI (29.1 mg, 153 μmol) and **IV-5** (2.31 g, 11.4 mmol) in 76 mL of a 1:1 v/v mixture of THF and piperidine was stirred for 12 h under Ar. The mixture was extracted with Et_2O (76 mL), and the extracts were washed with sat aq. NH_4Cl (100 mL) and DI H_2O (100 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (25:75 v/v ethyl acetate/hexanes) to afford the title compound as a yellow crystalline solid (2.24 g, 88% yield). m.p. = 146-147 ºC. ^{1}H NMR ($CDCl_3$): δ 0.91 (t, ^3J = 7 Hz, 3 H, CH_3), 1.31-1.50 (m, 6 H, alkyl-CH_2), 1.74-1.83 (m, 2 H, alkyl-CH_2), 3.97 (t, 2 H, ^3J = 7 Hz, OCH_2), 4.50 (s, 1 H, ≡C-CH_2), 4.51 (s, 1 H, ≡C-CH_2), 6.85-7.46 (m, 8 H, Ar-H). ^{13}CNMR ($CDCl_3$): δ 14.0 (CH_3), 22.6 (CH_2), 25.7 (CH_2), 29.1 (CH_2), 31.6 (CH_2), 51.7 (CH_2), 68.1 (OCH_2), 85.5 (≡C), 87.6 (≡C), 88.8 (≡C), 91.5 (≡C), 114.6, 114.7, 121.8, 123.9, 131.3, 131.6, 133.1, 159.4. IR (AT-IR, neat): 3319, 2953, 2920, 2870, 1605, 1512, 1246, 1027, 835 cm^{-1}. MS (EI): m/z (%) 332.1 (100) [M^+], 248.1 (65), 43 (15). HRMS calculated for $C_{23}H_{24}O_2$, 332.17763; found 332.17745, Δ = 0.5 ppm.



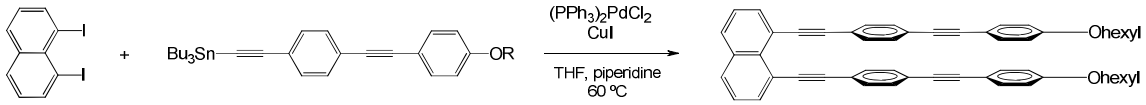
IV-7 **IV-8**: 48%

(4-(4-Hexyloxyphenylethynyl)phenyl)acetylene, IV-8. MnO_2 (5.75 g, 66.2 mmol) and potassium hydroxide (3.71 g, 66.2 mmol) were added in four separate portions to a solution of **IV-7** (2.20 g, 6.62 mmol) in Et_2O (100 mL) and the mixture was stirred at room temperature. The progress of the reaction was monitored by TLC until no more starting material was observed. The mixture was extracted in Et_2O (300 mL) and the solution was filtered through a plug of silica with a fritted funnel. The solvent was removed under reduced pressure to afford the title compound as a yellow solid (0.958 g, 48%). m.p. = 100-101 ºC. ^{1}H NMR ($CDCl_3$): δ 0.91 (t, ^3J = 7 Hz, 3 H, CH_3), 1.32-1.50 (m, 6 H, alkyl-CH_2), 1.74-1.83 (m, 2 H, alkyl-CH_2), 3.17 (s, 1 H, ≡C-H), 3.97 (t, ^3J = 7 Hz, 2 H, OCH_2), 6.85-7.46 (m, 8 H, Ar-H). ^{13}CNMR ($CDCl_3$): δ 14.0, 22.6, 25.7, 29.1, 31.6, 68.1, 78.7, 83.4, 87.5, 91.6, 114.5, 114.6, 121.4, 124.2, 131.2, 131.3, 132.0, 159.4. IR (AT-IR, neat): 3272, 3036, 2927, 2870, 2210, 1605, 1512, 1246, 1027, 838, 615, 536 cm^{-1}. MS (EI): m/z (%) 302.1 (70) [M^+], 218.1 (100), 189.1 (20), 43 (10). HRMS calculated for $C_{22}H_{22}O$, 302.16707; found 302.16413, Δ = 9.7 ppm.



IV-8 **IV-9**

((4-(4-Hexyloxyphenylethynyl)phenyl)ethynyl)tributyl stannane, IV-9. A solution of 1-butyllithium (2.2 M in hexanes, 0.61 mL, 1.6 mmol) was added drop-wise to a solution of **IV-8** (0.450 g, 1.49 mmol) in 15 mL THF at -78 ºC under Ar. The mixture was stirred for 30 min, tri-*n*-butyltin(IV) chloride (0.533 g, 1.64 mmol) was added dropwise, and the mixture was left to warm to room temperature and stirred overnight. The product mixture was used without any further purification. MS (EI): m/z (%) 592.2 (10)[M^+], 539.1 (100), 251 (70). HRMS calculated for $C_{34}H_{48}OSn$ 592.27272; found 592.27369, Δ = 1.6 ppm.



IV-9 **IV-10**: 34%

1,8-(4-(4-Hexyloxyphenylethynyl)phenyl)ethynyl)naphthalene, IV-10. To the previous crude product mixture was added 1,8-Diiodonaphthalene (190 mg, 0.500 mmol), tetrakis(triphenylphosphine)palladium(0) (57 mg, 49 µmol, 5 mol% per iodide), lithium chloride (85 mg, 2.0 mmol, 2 eq per iodide) and butylated hydroxytoluene (1 mg, 5 µmol, 0.5 mol % per iodide) was stirred at 60 ºC for 12 h. The mixture was diluted with Et_2O (100 mL) and washed with sat. aq. NH_4Cl (100 mL), and H_2O (100 mL). The solvent was removed under reduced pressure and the residue was subjected to column

chromatography (25:75 v/v ethyl acetate/hexanes). After removal of the solvent from the fractions the residue was triturated with MeOH and hexanes to afford the title compound as a pale yellow crystalline solid (125 mg, 34% yield). m.p. = 132 -135 ºC. ^{1}H NMR (CD_2Cl_2): δ 0.83 (t, ^{3}J = 7 Hz, 3 H, CH_3), 1.22-1.42 (m, 6 H, alkyl-CH_2), 1.64-1.73 (m, 2 H, alkyl-CH_2), 3.86 (t, ^{3}J = 7 Hz, OCH_2), 6.79 (d, J = 9 Hz, 4 H, Ar-H), 7.20-7.25 (m, 4 H, Ar-H), 7.39 (d, ^{3}J = 9 Hz, 4 H, Ar-H), 7.49 (dd, ^{3}J = 8 Hz, ^{3}J = 8 Hz, 2 H, naphthyl H 3, 6), 7.87 (d, J = 8 Hz, 2 H, naphthyl-H), 7.88 (d, J = 8 Hz, 2 H, naphthyl-H). ^{13}C NMR ($CDCl_3$): δ 13.9 (CH_3), 22.7 (CH_2), 25.7 (CH_2), 29.2 (CH_2), 31.7 (CH_2), 68.2 (OCH_2), 87.8 (≡C), 91.3 (≡C), 91.4 (≡C), 96.4 (≡C), 114.5, 114.7, 120.5, 123.1, 123.3, 125.8, 130.0, 131.0, 131.4, 133.1, 134.2, 135.0, 159.5. IR (AT-IR, neat): 3046, 2930, 2857, 2209, 1605, 1512, 1250, 835, 765 cm^{-1}. MS (FAB): m/z (%) 729.1 (70) [M^{+}+ H], 612.9 (20), 460 (100). HRMS calculated for $C_{54}H_{48}O$, 728.36543; found 728.36481, Δ = 0.9 ppm.

4.3 Results and Discussion

4.3.1 Synthesis of Alkyne Arms

The synthesis of symmetrical π-stacked oligomers was devised to include a sole alkoxy group on the terminus of each conjugated oligomer. The alkoxy group was introduced by alkylation of 4-iodophenol with a bromoalkane using a Williamson ether synthesis. After workup, propargyl alcohol was added to the crude product and Sonogashira coupling[16] was used to obtain gram quantities of alcohols **IV-1** and **IV-4** in high yield requiring just one chromatographic separation. The synthesis benefits from the

polarity of the propargyl substituent, which facilitates simple separation of unreacted starting material from propargylated product. These alcohols were oxidized in the presence of manganese dioxide and potassium hydroxide to afford terminal alkynes **IV-2** and **IV-5**.

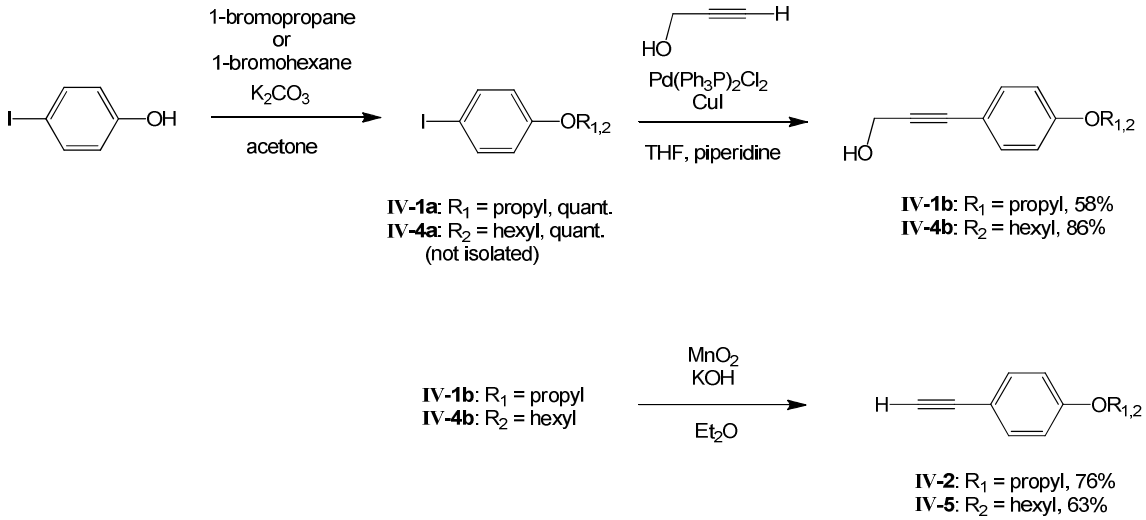


Figure 4.1. Synthesis of **IV-2** and **IV-5** which are 1,4-substituted phenylene ethynylenes that bear a sole alkoxy group.

In the interest of developing extended oligomers with a single terminal alkoxy group, a synthetic scheme was devised to extend the oligomer by one phenylene ethynylene unit. For this, 1,4-diiodobenzene was exposed to 1 equivalent of propargyl alcohol to prepare bifunctional alcohol **IV-6.** This iodide was then combined with alkyne **IV-5** to give dimer alcohol **IV-7,** which was then oxidized to terminal alkyne dimer **IV-8**, Figure 4.2.

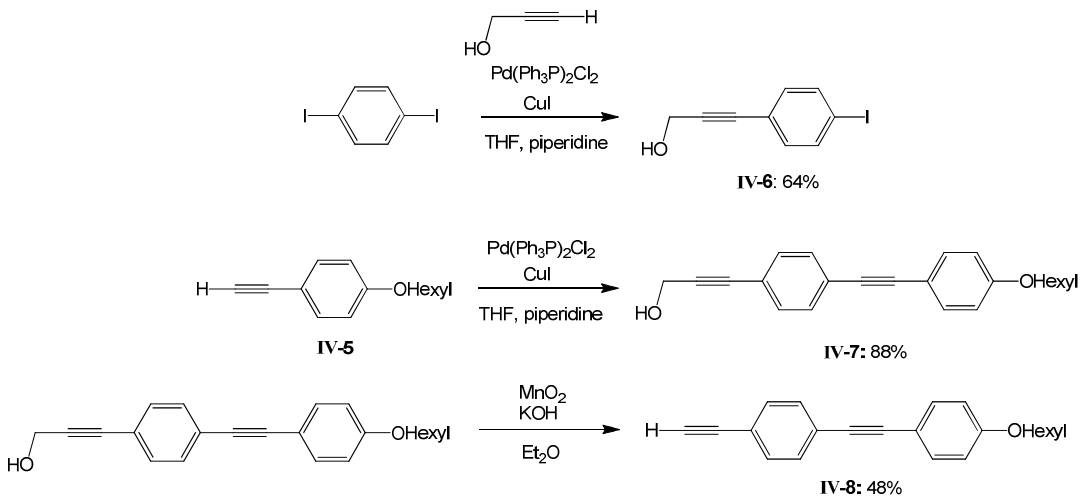


Figure 4.2. Synthetic scheme to afford a 1,4-substituted phenylene ethynylene oligomer with two PE repeat units bearing a sole alkoxy group at the terminus.

4.3.2 Coupling of Oligo(PE) Arms to Naphthalene

Alkyne **IV-2** was coupled to 1,8-diiodonaphthalene using Sonogashira reaction conditions at 70 ºC, Figure 4.3. The product was purified by column chromatography and the product underwent additional purification by recrystallization from methanol to afford a naphthalene-bridged PE monomer, IV-**3** in 47% yield.

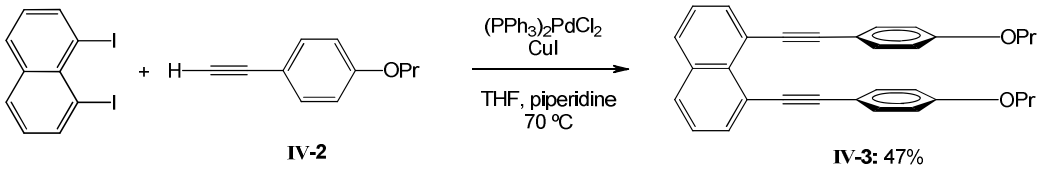


Figure 4.3. Coupling of **IV-2** to 1,8-diiodonaphthalene to afford naphthalene-bridged 1,4-substituted PE, compound **IV-3**.

With the assistance of Glen Brizius and Whitney Komorner, variants of compound **IV-10** were investigated by incorporating other alkoxy groups such as hexadecyl, triethylene glycol, and propyl chains. The main issue from use of such side

chains was the inability to separate homo-coupled product (1,3-di-ynes formed by oxidative coupling of the terminal alkyne arms) from the final product. Both the hexadecyl and propyl substituted compounds were relatively insoluble, and the triethylene glycol analog was so polar it negated any practical separation by column chromatography. Thus, an alkyl chain of moderate-length was explored with the assumption it would provide suitable solubility in moderately polar solvents. An independent experiment identified that Stille coupling produced less homo-coupled product than attempts to prepare these compounds by Sonogashira couplings. Accordingly as shown in Figure 4.4, alkyne dimer **IV-8** was treated with tri-*n*-butyltin chloride to afford stannane **IV-9**. This stannane was then used in Stille coupling to 1,8-diiodonaphthalene in the presence of $Pd(Ph_3)_4$ to furnish compound **IV-10** in 34% yield.

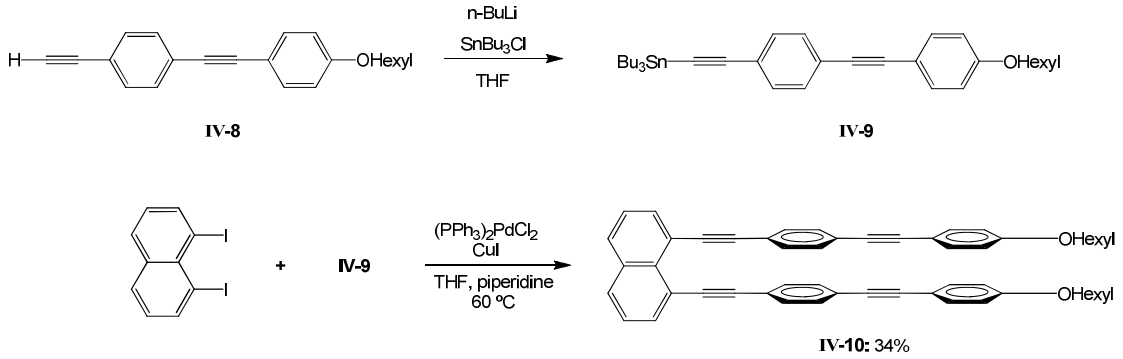


Figure 4.4. Formation of stannane **IV-9** and subsequent coupling to 1,8-diiodonaphthalene using Stille coupling to afford naphthalene bridged 1, 4-substituted PE dimer, compound **IV-10**.

4.3.3. Structural Characterization: ^{1}H NMR and ^{13}C NMR Spectroscopy

The disubstituted naphthalene PE oligomers were characterized by ^{1}HNMR in $CDCl_3$ or CD_2Cl_2. The spectrum of naphthalene-bridged 1,4-substituted PE dimer, **IV-10** is shown in Figure 4.5. The protons on the C3 and C6 positions on the naphthalene

appear as a triplet, at δ 7.5 ppm arising from coupling to both adjacent protons with coupling constants of 8 Hz, consistent for a 1,8-disubstituted naphthalene. However, the protons on C2, 4, 5, and 7 appear as doublets at δ 7.9 which is quite different from the naphthalenes substituted with dialkoxy oligo(PE)s (Chapter 2) where these doublets are separated by a chemical shift of 0.07 ppm.

The protons on the 1,4-dialkyne substituted phenylene ring adjacent to the naphthalene appear as a singlet at δ 7.32 ppm, while the protons on the phenylene ring bearing the terminal alkoxy group appear as a pair of doublets at δ 6.79 and δ 7.39 ppm with a coupling constants of $J = 9$ Hz.

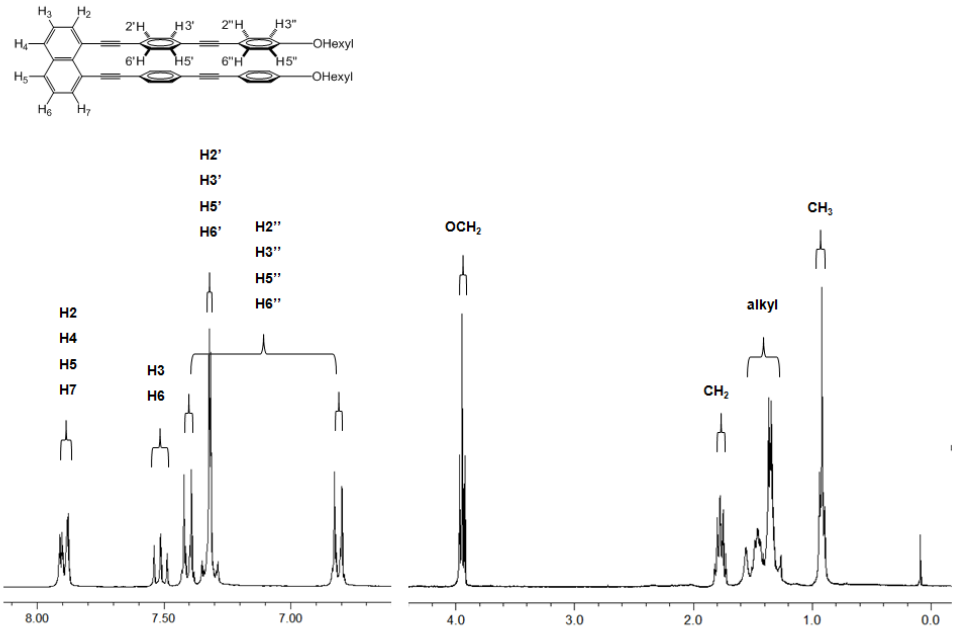


Figure 4.5. ^{1}HNMR (300 MHz in CD_2Cl_2) of compound **IV-10**. Note that the two regions are not the same y-scale.

4.3.4. X-ray Structural Analysis

Crystals of **IV-3** which were suitable for X-ray analysis were grown in 30:70 ethyl acetate:hexanes by slow solvent evaporation. Analysis of the crystal structure in Figure 4.11(A) shows that the angle of C14-C18-C27 is 117º. This is a contrast from the diphenylnaphthalene structure reported by House where an angle closer to 90º was expected.[17] Further deviations from the expected angles are evident from the C13-C1-C8 angle of 97º Figure 4.11(B) which was also expected to be approximately 90º. These deviations of the phenylene units appear to originate from the electron-rich alkoxy units which can be much more pronounced compared to the dialkoxy phenylene ethynylenes in structure **II-8**. The naphthalene in structure **IV-3** is highly planarized, experiencing little if any deformations unlike the naphthalene in structure **II-8**. Also, the C16-C24 inter-

atomic distance of 3.9 Å between the two stacked phenylene rings depicted in Figure 4.11(A) is within a π-stacking distance suggesting there are significant π-π interactions within this molecule.

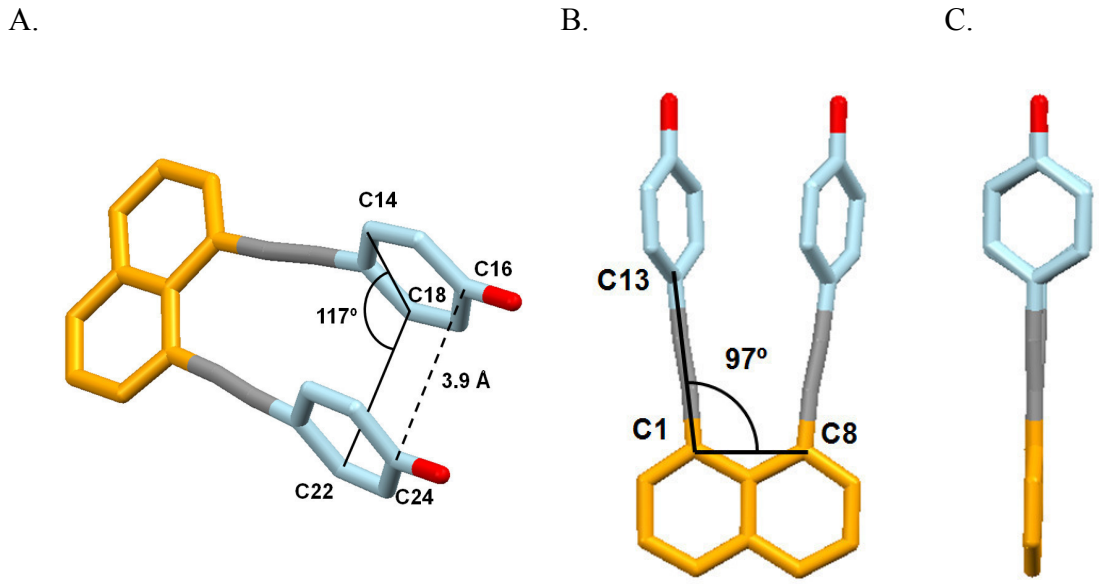


Figure 4.6. X-ray crystal structure of **IV-3.**

The molecular packing of **IV-3** shown in Figure 4.12 is *C2subC* where there are six molecules per unit cell. It appears there are two pairs of molecules where the C16 on the phenylene is 4.8 Å apart from the C4 of the naphthalene (Figure 4.13). These interactions are similar to the herringbone crystal packing of arenes associated with pentacene.[18]

A. B.

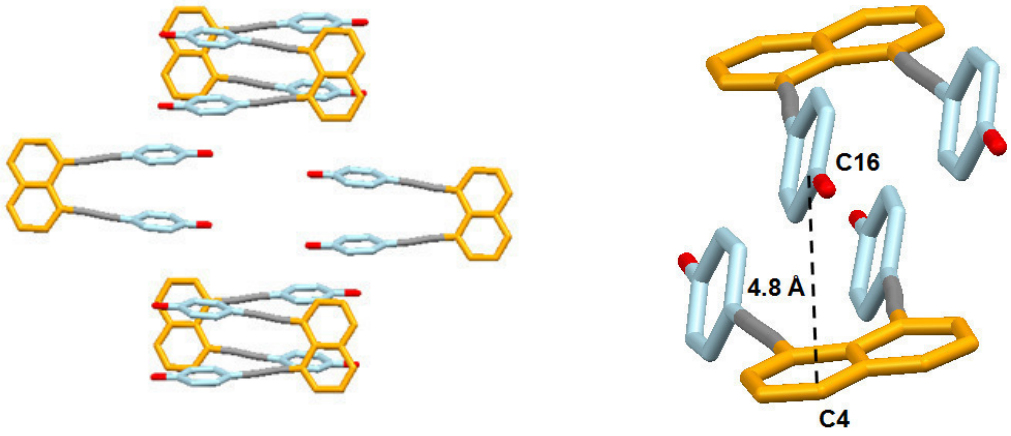


Figure 4.7. Crystal packing structure of **IV-3**.

4.3.5. Electrochemistry of Alkyne Arms and Naphthyl-Bridged Oligo(PE)s

Voltammograms of oligo(PE) alkynes **IV-2** and **IV-8** and naphthalene-bridged **IV-3** and **IV-10** were collected by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), Tables 4.1 and 4.2, and Figures 4.8 and 4.9. Only **IV-8** and **IV-3** were oxidized under the experimental conditions. Nonetheless, this provided us with a comparison between an alkyne oligomer and naphthyl-bridged oligomer each bearing one alkoxy group per oligomer. Alkyne PE dimer **IV-8** shows a single irreversible oxidation wave with a peak potential of +1.98 mV versus Fc/Fc^{+}. The oxidative wave for the analogous naphthyl-bridged PE monomer **IV-3** is split, with peaks at +1.75 and +1.82 mV. This data is similar to the laterally dialkoxy substituted PEs in which the unbridged oligomer gave one redox wave and the naphthyl-bridged oligomers gave two redox waves. However, the difference between the first and second oxidation peaks of **IV-3** are

less than 100 mV which could be an effect of the π-π interactions on the electronic properties of the molecule.[19-20]

Table 4.1. Electrochemical CV data for alkyne **IV-8** and naphthyl-bridged PE oligomer **IV-3**.

	Potential / V			
Compound	I_{ox}	II_{ox}	I_{red}	II_{red}
IV-8	1.98	-	-	-
IV-3	1.75	1.82	1.77	1.30

Table 4.2. Electrochemical DPV data for alkyne **IV-8** and naphthyl bridged PE oligomer **IV-3**.

	Potential / V	
Compound	I_{ox}	II_{ox}
IV-8	1.98	-
IV-3	1.72	1.83

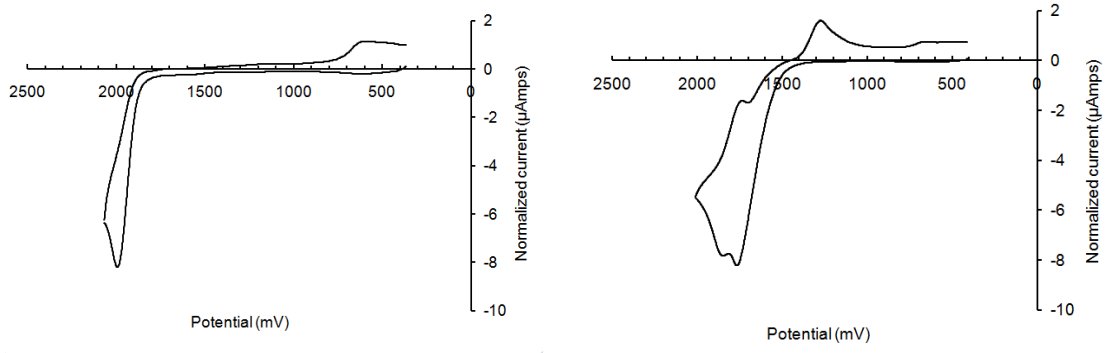


Figure 4.8. CV of unstacked alkyne **IV-8** and naphthyl-bridged PE monomer **IV-3**. Measurements were recorded at 100 mV/s with gold working electrode and silver reference electrode in 0.1 M NBu_4PF_6. All potentials are referenced to Fc/Fc^+ at 450 mV.

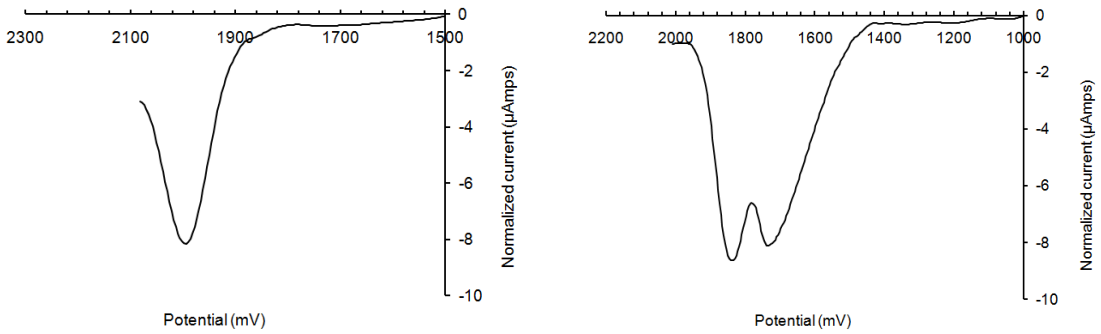


Figure 4.9. DPV of alkyne **IV-8** and naphthyl-bridged PE monomer **IV-3**. Measurements were recorded at 100 mV/s with a gold working electrode and silver reference electrode in 0.1 M NBu_4PF_6. All potentials are referenced to Fc/Fc^+ at 450 mV.

4.3.6. UV-vis and Florescence Measurements of Alkynes and Naphthyl-Bridged Oligo(PE)s

The UV absorbance and fluorescence spectra of alkynes **IV-2** and **IV-8** and naphthyl-bridged oligomers **IV-3** and **IV-10** were recorded. Data is presented in Table 4.3, and Figures 4.10 and 4.11**.** A comparison of alkyne **IV-2** with the corresponding naphthyl-bridged monomer **IV-3** indicates that the molar absorptivity value dramatically increases from 0.9×10^3 to 56.5×10^3 upon stacking, the absorbance becomes more red-shifted. Interestingly, the fluorescence wavelengths of **IV-3** and **IV-10** are very similar: The naphthyl-bridged monomer **IV-3** fluoresces at a wavelength which is only 4 nm higher than the alkyne **IV-2**, and there is a decrease in the Stokes shift by 19 nm. This could be due to the "phane state" as reported by Bazan having a predominating effect over the fluorescence. This type of emission can persist if an unstacked oligomer is the major absorbing species and there is subsequent intermolecular radiative and non-radiative energy transfer to a lower-energy chromophore that is formed amongst π-stacked aromatic units.

Alkyne PE dimer **IV-8** has a lower molar absorptivity of 30.0 $\times 10^3$ $M^{-1}cm^{-1}$ at 313 nm than naphthyl-bridged PE dimer **IV-10**. This alkyne has a second peak at the longer wavelength at 325nm which could be due to vibronic coupling. A comparison of **IV-8** with **IV-10** finds that the naphthyl-bridged oligomer has a new absorbance maximum red-shifted from the corresponding alkyne but retains a similar absorbance maximum at 313 nm. This could be due to the fact that the "phane-state" of this molecule is not continuous and each set of overlapping phenylene units makes up two different absorbing species. The fluorescence of naphthyl-bridged dimer **IV-10** is more red-shifted than alkyne dimer **IV-8;** and much like **IV-3**, the Stokes shift decreases upon stacking the oligomers, Figure **4.10**.

Table 4.3. UV-vis absorbance and fluorescence data for alkynes **IV-2** and **IV-8** as well as naphthyl-bridged PE oligomers **IV-3** and **IV-10**.

Oligomer	$\lambda_{abs\ solution}$ (nm)	Molar absorptivity ε /$\times 10^3$	$\lambda_{em\ solution}$ (nm)	Stokes shift(nm)
IV-2	323	0.9	408	85
IV-3	346	56.5	412	66
IV-8	313	30.0	376	63
IV-10	356	50.1	406	50

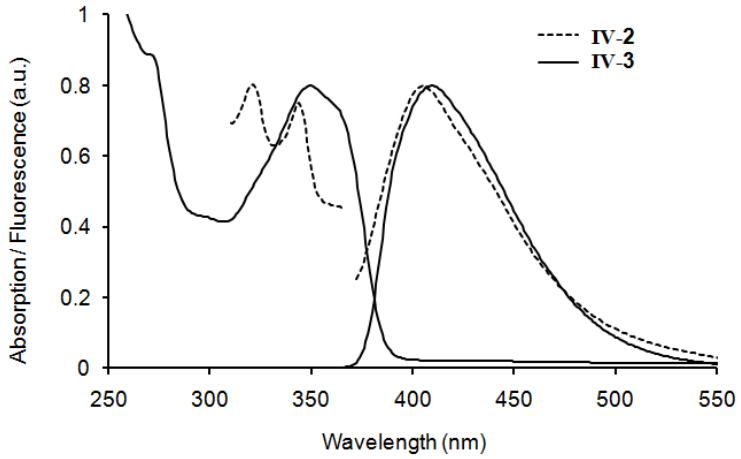


Figure 4.10. UV-vis and fluorescence spectrum of alkyne PE monomer **IV-2** (dashed) and naphthyl-bridged PE monomer **IV-3** (solid) in CH_2Cl_2 at ~10^{-6} M.

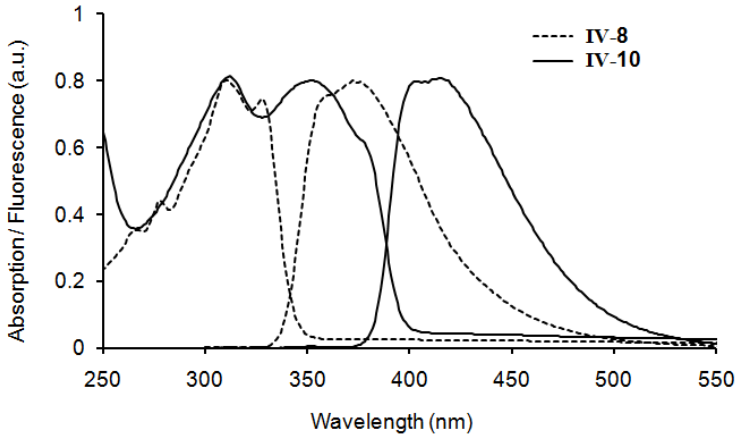


Figure 4.11. UV-vis and fluorescence spectrum of alkyne PE dimer **IV-8** (dashed) and naphthyl-bridged PE dimer **IV-10** (solid) in CH_2Cl_2 at ~10^{-6} M.

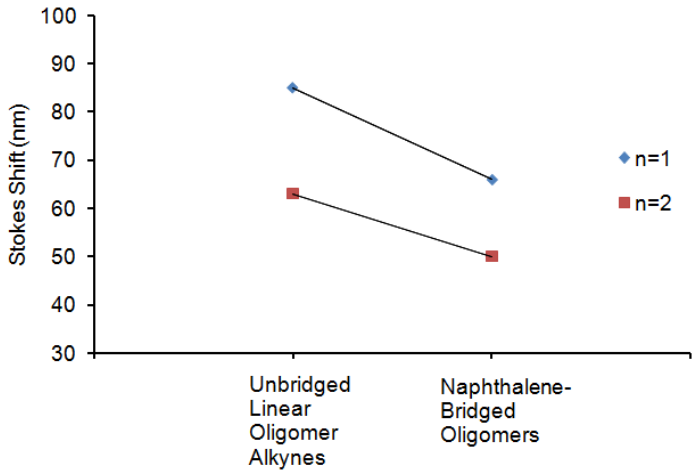


Figure 4.12. Plot of the number of oligomers with the corresponding Stokes shift observed. The legend corresponds to the number of consecutive PE repeat units.

4.4. Conclusions

We have reported the synthesis of 1,4-substituted PE oligomers with a single alkoxy group at the terminus that have been coupled to a naphthalene bridging unit to study π-stacking interactions. In contrast to the naphthalene-bridged dialkoxy PE oligomers reported in Chapter 2, these terminal alkoxy-substituted oligomers demonstrate a high degree of π-stacking of the phenylene units. We have reported electrochemical and optical properties associated with these π-stacked oligomers. Crystal structures reveal structural properties of π-stacking that could aid in the design of new materials for high-mobility organic semiconductors.

4.5. References

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CHAPTER 5

SYNTHESIS AND CHARACTERIZATION OF NAPHTHYL-STACKED OLIGO(PHENYL ETHYNYLENE) MACROCYCLES

5.1. Introduction

Macrocycles are closed-ring structures generally made up of 10 atoms or more that can include aromatic rings to make up the enclosed structure.[1-2] Within these structures there can be a high degree of overlap amongst the aromatic units which can serve as a model for segments of overlapping aromatic units in conjugated polymers. Discerning the effect of such interactions on the material properties of these semiconducting materials is relevant to their performance in thin film electronic devices. To explore the interaction of conjugated oligomers we sought to incorporate oligo(phenylene ethynylene)s into a macrocyclic structure in which they are held together by a 1,8-disubstituted naphthalene unit. A common challenge to obtaining such macrocyclic structures is a direct synthesis that forms the product in high yield.

While attempts were made to prepare oligo(phenylene ethynylene)s in this fashion, we were also drawn to the possibility of forming 1,3-di-ynes by oxidative coupling of terminal alkynes. Previous work by Swager[3] and Bunz[4] has shown that di-ynes display a bent geometry in the preparation of an annulyne from 1,2-diethynylbenzene. Using 1,8-substituted naphthalene to make such an annulyne macrocycle structure will minimize the strain on the di-yne bond as the 1,8-substitution of the naphthalene provides a parallel geometry for the alkynes to bond with one another.

Our goal in designing a macrocycle composed of 1,8-substituted naphthalene and dialkoxy phenylene ethynylene oligomers to use the macrocyclic structure to tie the ends of the oligomers together and thereby minimize the deformations associated dialkoxy phenylenes, Chapter 2; and thereby obtain a product that has high degree of aromatic π-π interactions.

5.2. Experimental

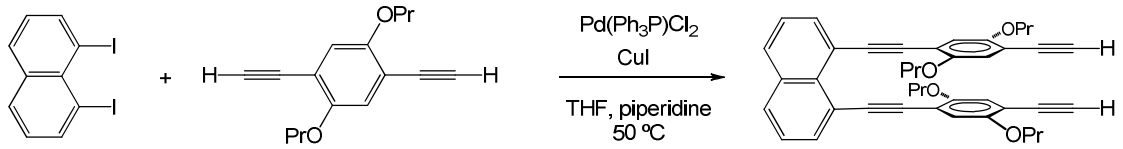
5.2.1 General Procedures

All reactions were conducted with distilled solvents in oven-dried and argon-charged glassware. All reagents were used as received from commercial suppliers without prior purification. Analytical thin layer chromatography (TLC) was performed on precoated aluminum-backed plates purchased from Sorbent Technologies (silica gel 60 F254; 0.25 mm thickness). Flash column chromatography was performed on silica gel 60 (230-400 mesh ASTM) from Sorbent Technologies. ^{1}H NMR (300 MHz) spectra were recorded on a Varian Gemini spectrometer. NMR spectra were measured in solutions of deuterated chloroform ($CDCl_3$) with tetramethylsilane as the internal standard and reported in parts per million (ppm). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet.

IR spectra were collected on a Nicolet 4700 FTIR with an ATR attachment from SmartOrbit Thermoelectronic Corp with samples as neat films. Mass spectra including high resolution were measured by EI on a Waters 70SE instrument or MALDI Micromass TofSpec2E instrument.

5.2.2. Synthetic Procedures

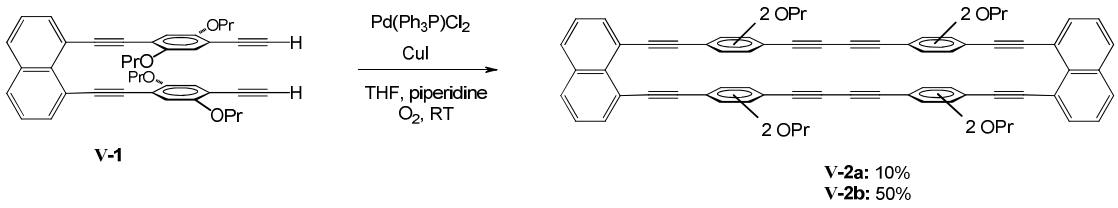
1,4-diethynyl-2,5-dipropyloxybenzene was prepared exactly according to a literature procedure.[5]



V-1: 53%

1,8-(4-Ethynyl-2,5-dipropyloxyphenylethynyl)naphthalene, V-1. 1,8-Diiodonaphthalene (380 mg, 1.00 mmol), 1,4-diethynyl-2,5-dipropyloxybenzene (969 mg, 4.00 mmol), $Pd(Ph_3P)_2Cl_2$ (14 mg, 0.02 mmol), and CuI (8 mg, 0.04 mmol) were added to 20 mL of a 1:1 v/v mixture of THF and piperidine under Ar and the mixture was stirred at 50 ºC for 4 h. The mixture was extracted into Et_2O (100 mL) and washed with sat. aq. NH_4Cl (100 mL) and DI H_2O (100 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (10:90 v/v ethyl acetate/hexanes) to afford the title compound as a beige solid (320 mg, 53% yield). ^{1}H NMR ($CDCl_3$): δ 0.97 (t, J = 7 Hz, 6 H, CH_3), 1.09 (t, J = 7 Hz, 6 H, CH_3), 1.61-1.74 (m, 4 H, CH_2), 1.81-1.93 (m, 4 H, CH_2), 3.34 (s, 2 H, ≡C-H), 3.38 (t, J = 7 Hz, 4 H, OCH_2), 3.89 (t, J = 7 Hz, 4 H, OCH_2), 6.80 (s, 2 H, Ar-H), 6.93 (s, 2 H, Ar-H), 7.46 (dd, J = 8 Hz, J = 8Hz, 2 H, naphthyl-H 3, 6), 7.82 (d, J = 8 Hz, 2 H, naphthyl-H), 7.90 (d, J = 8 Hz, 2 H, naphthyl-H). ^{13}CNMR ($CDCl_3$): δ 10.3 (CH_3), 10.5 (CH_3), 22.4 (CH_2), 22.6 (CH_2), 70.2 (OCH_2), 70.8 (OCH_2), 80.0 (≡C), 82.3 (≡C), 93.2, 95.7, 112.1, 115.0, 116.4, 117.0, 121.0, 125.6, 129.6, 130.9, 133.9, 135.0, 153.2, 153.9. IR (AT-IR, neat): 3285,

2957, 2933, 2871, 2100, 1602, 1559, 1500, 1390, 1271, 1219 cm^{-1}. MS (EI): m/z (%) 608.3(100) [M^+], 565.3 (95) [M^+- OC_3H_7], 337.1 (60). HRMS calculated for $C_{42}H_{40}O_4$, 608.2927; found 608.2928, Δ = 0.2 ppm.



V-1

V-2a: 10%
V-2b: 50%

Di-1,8-(4-ethynyl-2,5-dipropyloxyphenylethynyl)naphthalene), V-2a, b. Compound **V-1** (200 mg, 0.329 mmol), $Pd(Ph_3P)_2Cl_2$ (23 mg, 0.03 mmol) and CuI (6 mg, 0.03 mmol) were dissolved in 20 mL of a 3:1 v/v mixture of THF and piperidine, and O_2 gas was bubbled through the stirred mixture for 30 min. The mixture was extracted into Et_2O (100 mL) and washed with sat. aq. NH_4Cl (100 mL) and DI H_2O (100 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (silica with eluent hexanes graduating to 30:70 v/v ethyl acetate/hexanes) to afford two separate components, the first (**V-2a**) was a yellow oil (20 mg, 10% yield) and the second component (**V-2b**) was isolated as a radiant light green oil (100 mg, 50% yield).

V-2a (**R_F = 0.25,** 25:75 v/v ethyl acetate/hexanes)**:** ^{1}H NMR ($CDCl_3$): δ 1.04-1.11 (m, 24 H, CH_3), 1.73-1.90 (m, 16 H, CH_2), 3.61 (t, *J* = 7 Hz, 8 H, OCH_2) 3.82 (t, *J* = 7 Hz, 8 H, OCH_2), 6.69 (s, 4 H, Ar-H), 6.75 (s, 4 H, Ar-H), 7.46 (t, *J* = 7 Hz, 4 H, naphthyl-H 3,6), 7.80-7.86 (m, 8 H, naphthyl-H). IR (AT-IR, neat): 2914, 2842, 2152, 2023, 1261, 1214,

1014 cm^{-1}. MS (MALDI): m/z (%) 1321.5(100) [M^++Ag]. HRMS calculated for $C_{84}H_{76}O_8Na$, 1235.553; found 1235.538, Δ = 15 ppm.

V-2b (**R_F = 0.20,** 25:75 v/v ethyl acetate/hexanes)**:** ^{1}H NMR ($CDCl_3$): δ 1.01 (t, *J* = 7 Hz, 12 H, CH_3) 1.09 (t, *J* = 7 Hz, 12 H, CH_3) 1.65-1.75 (m, 8 H, CH_2), 1.82-1.95 (m, 8 H, CH_2), 3.44 (t, *J* = 7 Hz, 8 H, OCH_2), 3.93 (t, *J* = 7 Hz, 8 H, OCH_2), 6.82 (s, 4 H, Ar-H), 6.98 (s, 4 H, Ar-H), 7.48 (t, *J* = 7 Hz, 4 H, naphthyl-H 3, 6). IR (AT-IR, neat): 2963, 2917, 2844, 2120, 1499, 1270, 1213 1060, 977 cm^{-1}.

5.3 Results and Discussion

5.3.1 Synthesis of Macrocycle

In the development of macrocycle **V-2**, many synthetic schemes were explored to incorporate oligo(phenylene ethynylenes) as overlapping segments of conjugated chains to make π-stacks. Our attempts at making a ring-closed structure by cross coupling terminal alkynes on phenylene ethynylenes with aryl iodides on the naphthalene failed likely due to the high degree of strain associated with making a ring-closed product. ^{1}H NMR from the product mixtures of these attempts showed only low-molecular weight oligomers, approximately 2 or 3 repeat units.

Therefore, a strategy was devised to form a macrocycle using a disubstituted naphthalene structure with 1,4-dipropyloxy-2,5-diethynylbenzene **V-1** (Figure 5.1). Unfortunately, attempts to form a macrocycle of **V-1** through ring-closure with 1,8-diiodonaphthalene did not afford any isolable macrocycle product, suggesting that such a highly strained structure would not be accessible through cross-coupling conditions.

Earlier reports by Swager[3] and Bunz[4] identified the Eglinton reaction as an alkyne-alkyne coupling reaction capable of forming highly strained macrocycles. Their approach used a dialkyne with Cu(I)Cl and nitrobenzene at room temperature in the presence of oxygen gas to undergo oxidative coupling to give a ring-closed structure. Initial attempts to form a macrocycle using this procedure resulted in incomplete conversion of the dialkyne. However, the reaction did proceed in high yield upon changing the conditions to $Pd(Ph_3P)_2Cl_2$, CuI, in a mixture of THF and piperdine while bubbling through oxygen; which, has previously been reported by Xie[6] and Lahti[7]. The reaction was monitored for 30 min by TLC during which the starting material was consumed and two highly fluorescent spots appeared (R_f = 0.25 and 0.20 in 25:75 v/v EtOAc:hexanes). The two components were isolated by gradient column chromatography (silica stationary phase with mobile phase hexanes graduating to 30:70 EtOAc:Hex) allowing for isolation of 20 mg of the first component (10% yield) and a 100 mg of a second component (50% yield).

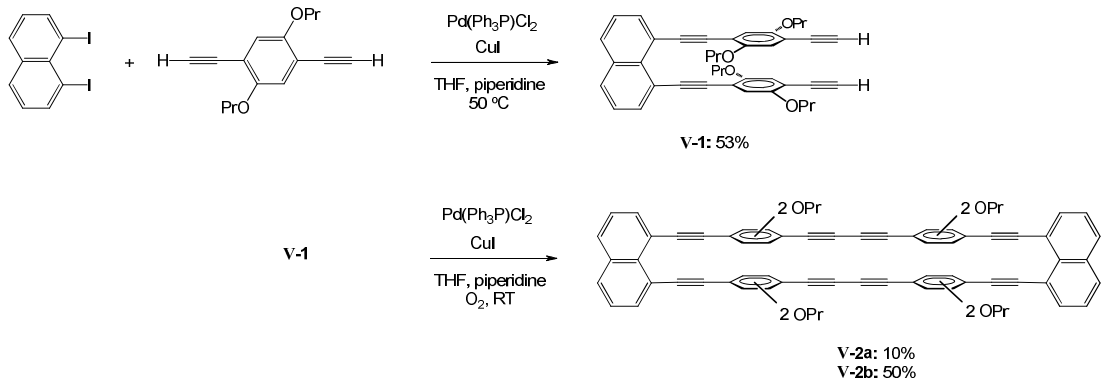


Figure 5.1. Synthetic route for the preparation of macrocycle **V-2a, V-2b**.

5.3.2. Characterization by ^{1}H NMR Spectroscopy and MALDI Mass Spectrometry

The ^{1}H NMR spectra of naphthalene-bridged dialkyne **V-1** and compounds **V-2a**, and **V-2b** are given in Figure 5.2. In the spectrum of **V-1**, the alkyne protons appear at δ 3.34 ppm This signal is absent on the spectra of **V-2a** and **V-2b**, which supports formation of the di-yne bond. Aromatic protons on the phenylenes of **V-1** appear as two separate singlets at δ 6.80 and δ 6.93 ppm. For **V-2a**, these protons are shifted further upfield to δ 6.69 and δ 6.75 ppm, and for **V-2b**, are at chemical shifts of δ 6.82 and δ 6.98 ppm, which is close to that of the starting material. This trend is continued for other signals in compound **V-2b** where signals assigned to the naphthalene and propyl moieties closely match those of **V-1**.

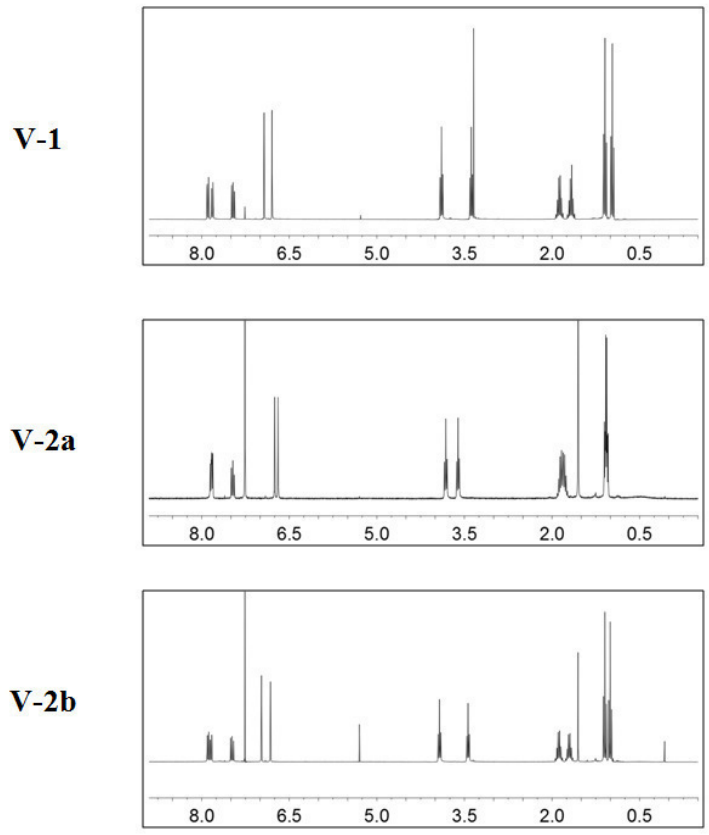


Figure 5.2. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **V-1** and **V-2a** and **V-2b**.

Mass spectra were collected for compound **V-2a** (Figure 5.3). Samples were prepared in a matrix of dithranol. The spectrum of **V-2a** returned a weak signal for the molecular ion. However, upon addition of silver triflate, the signal of a single peak with a mass of 1321.5 amu was amplified which was consistent with the molecular ion plus silver. Mass spectral analysis for compound **V-2b** was not available as the molecular ion could not be detected by MALDI.

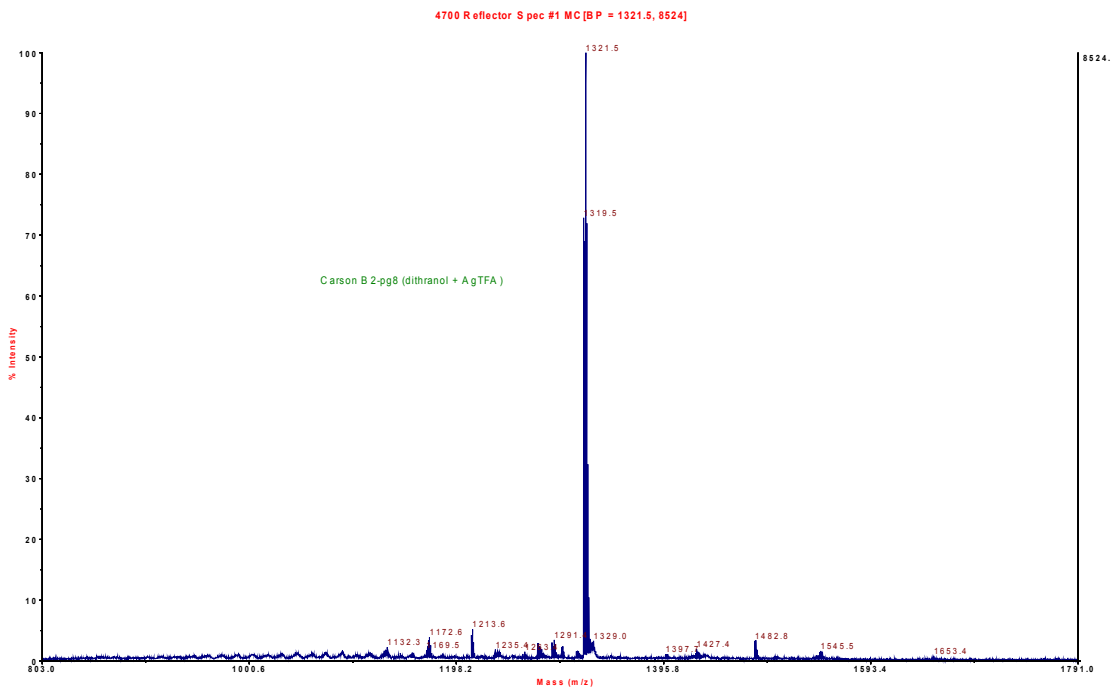


Figure 5.3. MALDI spectrum of **V-2a**, sample was prepared in a matrix of dithranol and silver trifluoroacetate to give the molecular ion plus silver [M+Ag^+].

5.3.3. Structural Analysis of Macrocycle

We suggest that **V-2a** and **V-2b** are two possible configurations the alkoxy units can adopt- eclipsing or staggered as shown in Figure 5.4. From crystal structures of dialkoxy phenylene ethynylenes with a 1,8-naphthalene bridgehead such as **II-8** and **III-4**, it appears dialkoxy PEs are more likely to adopt a staggered configuration; therefore the probability is low for the formation of eclipsing configurations such as E1-3. In Figure 5.4, there are two possible structures that from staggered configurations- one where the alkoxy units are symmetric, S1, and another where the PE units are oriented asymmetrically, S2. In the structure of S2, the alkoxy units are evenly dispersed which should afford a structure that is more energetically favored over the structure of S1 where steric strain could arise from the low proximal distance of the alkoxy substituents. Macrocycle **V-2a** is much less soluble which could originate from strain associated from

the low proximal distance of the alkoxy units such as those in conformation S1. Therefore, conformation S2 would appear to be the more thermodynamically favored product and the most probable identity of the major product, **V-2b**.

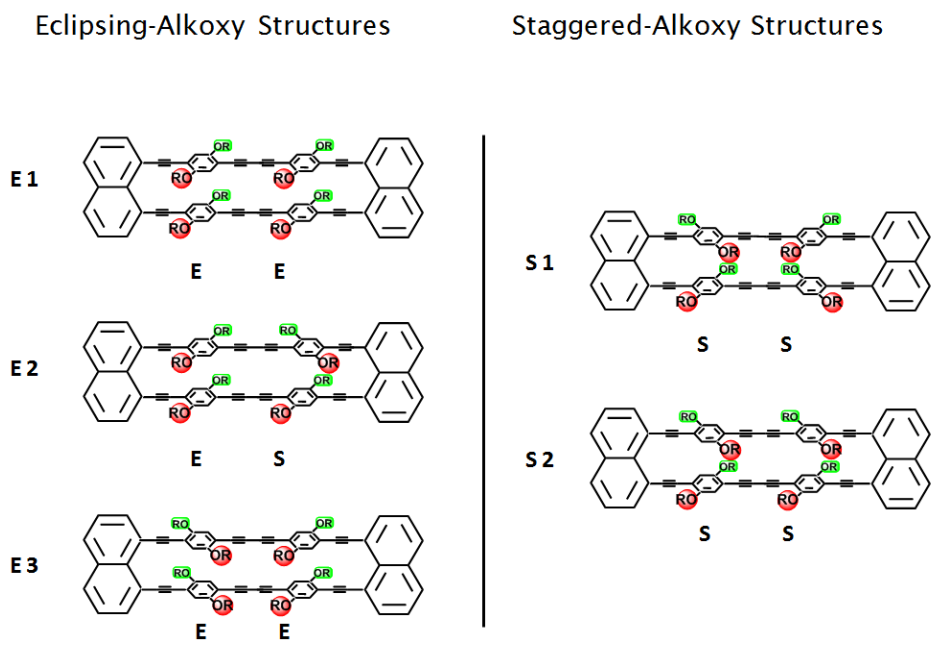


Figure 5.4. Five possible conformational isomers of macrocycles **V-2a** and **b**.

5.3.4. UV-vis and Fluorescence Spectroscopy

UV-vis and fluorescence spectra were recorded for the dialkyne **V-1** and macrocycles **V-2a** and **b**, Table 5.1 and Figure 5.5. The UV-vis spectra of both macrocycles **V-2a** and **b** are more red-shifted from dialkyne V-1 where macrocycle **V-2b** is the most red-shifted at 414 nm. Macrocycles **V-2a** and **b** both have an emission about 460 nm; however, macrocycle has a very weak fluorescence which is evident from the

low molar absorptivity. Macrocycle **V-2b** has a sharp, intense fluorescence which could be due to planarization of the oligomers within the structure of the macrocycle.

Table 5.1. UV-vis absorbance and fluorescence data for dialkyne **V-1** and macrocycles **V-2a** and **b**.

Compound	$\lambda_{abs\ solution}$ (nm)	Molar absorptivity $\varepsilon /\times 10^3$	$\lambda_{em\ solution}$ (nm)	Stokes shift(nm)
V-1	379	55.3	440	61
V-2a	399	1.61	460	61
V-2b	414	78.3	462	48

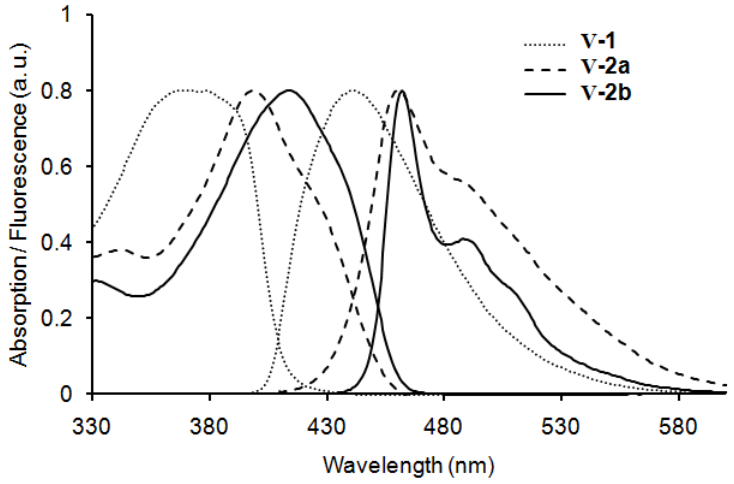


Figure 5.5. UV-vis and fluorescence spectrum of dialkyne **V-1** (dotted), macrocycle **V-2a** (dashed), and macrocycle **V-2b** (solid). Note the sharp fluorescence spectrum of macrocycle **V-2b**.

5.4. Conclusions

We have identified a route for oxidative coupling to form di-yne bonds with phenylene ethynylene dialkynes which was used to prepare novel macrocycle structures. The products were characterized by ^{1}H NMR, IR absorption spectroscopy, and mass spectrometry. We have identified possible configurations for the dialkoxy substituents and we suggest that the isolated compounds **V-2a** and **V-2b** are those with a staggered

arrangement of propyloxy side chains that correspond to structures S1 and S2 in Figure 5.4, respectively.

5.5. References

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APPENDIX A

CRYSTALLOGRAPHY DATA FOR REPORTED COMPOUNDS

Table A1. Crystallographic data for **1,8-(2,5-Dipropyloxyphenylethynyl)-naphthalene**, **II-8**.

Total Number of Atomic Coordinates: 82

Atom	X	Y	Z
C	0.839772	6.869895	5.549629
C	-0.065520	6.724772	6.569373
H	0.226620	6.831940	7.467719
C	-1.402717	6.423363	6.316171
H	-2.005145	6.295357	7.039357
C	-1.846230	6.313218	5.041491
H	-2.767785	6.147257	4.876736
C	-0.949188	6.442713	3.945439
C	-1.406666	6.318428	2.606591
H	-2.330637	6.173305	2.441837
C	-0.547983	6.402525	1.553896
H	-0.873414	6.368291	0.662487
C	0.822506	6.539461	1.800161
H	1.419513	6.555090	1.061367
C	1.342914	6.653327	3.085247
C	0.431848	6.669700	4.179564
C	2.165891	7.335032	5.950243
C	3.170351	7.770401	6.441038
C	4.337319	8.239260	7.098322
C	4.320173	8.356102	8.485729
C	5.463043	8.801890	9.151685
H	5.457386	8.895662	10.096856
C	6.598016	9.104787	8.442373
H	7.379982	9.392801	8.898483
C	6.602258	8.992410	7.075777
C	5.490087	8.571182	6.376870
H	5.508765	8.507179	5.428231
C	2.967304	8.378429	10.476659
H	3.175478	9.336984	10.608462
H	3.559774	7.842590	11.061104
C	1.515679	8.103812	10.804434
H	1.353523	8.319635	11.756542
H	1.337024	7.137814	10.679567
C	0.535731	8.907569	9.939038
H	0.675437	9.865380	10.091653
H	-0.384527	8.667186	10.178366
H	0.691641	8.702909	8.992133
C	7.928376	9.282656	5.058833
H	7.452574	10.046970	4.649548
H	7.563997	8.439455	4.692905

C	9.438512	9.380893	4.809100
H	9.705138	10.312657	5.010274
H	9.881789	8.804123	5.480258
C	9.924272	9.091392	3.697440
H	9.735895	8.151442	3.492798
H	10.894143	9.232793	3.719986
H	9.527249	9.662208	3.007205
C	2.782578	6.654071	3.201442
C	3.965573	6.523833	3.159820
C	5.383730	6.266332	3.097387
C	6.091689	5.889757	4.252403
H	5.650475	5.834685	5.093519
C	7.428356	5.602488	4.143145
C	8.063721	5.656816	2.934366
H	8.988104	5.450667	2.875401
C	7.364601	6.010321	1.800161
H	7.810175	6.030415	0.960779
C	6.039247	6.332568	1.867797
C	5.868075	6.720307	-0.497732
H	6.120913	5.799706	-0.761340
H	6.680740	7.286658	-0.501201
C	4.813649	7.282193	-1.444638
H	4.587915	8.206514	-1.174093
H	3.993147	6.733703	-1.385673
C	5.331345	7.282937	-2.904884
H	6.170761	7.784541	-2.953443
H	4.665928	7.704910	-3.487595
H	5.483484	6.360104	-3.197974
C	7.636532	5.358384	6.550296
H	7.045240	4.578441	6.708114
H	7.103868	6.187445	6.661289
C	8.839974	5.343500	7.526684
H	9.335928	4.492856	7.417426
H	9.453951	6.083999	7.294293
C	8.452733	5.475227	8.844721
H	7.971804	6.320660	8.960916
H	9.245188	5.468529	9.422229
H	7.864446	4.729518	9.089251
O	3.152616	8.007807	9.092720
O	7.815304	9.313169	6.479192
O	5.248130	6.725516	0.811633
O	8.222873	5.298846	5.237462

Table A2. Crystallographic data for **8-Dinaphthyl-(4-(2,5-dipropyloxyphenylethynyl)-2,5-(dipropyloxyphenylethynyl)-1-((2,5-dipropyloxyphenylethynyl)ethylene)**, **III-4**.

Total Number of Atomic Coordinates: 448

Atom	X	Y	Z
C	11.919748	1.732758	-3.042396
C	12.571917	2.205031	-4.173700
H	12.450595	3.108790	-4.438923
C	13.412203	1.365555	-4.934166
H	13.853209	1.699235	-5.706809
C	13.580109	0.087411	-4.555124
H	14.133181	-0.476105	-5.084777
C	12.962396	-0.454540	-3.390734
C	13.152235	-1.793249	-3.022809
H	13.689814	-2.352456	-3.570726
C	12.589685	-2.313240	-1.906858
H	12.720930	-3.228262	-1.688750
C	11.807417	-1.485791	-1.067512
H	11.426924	-1.847789	-0.275282
C	11.587223	-0.150801	-1.386204
C	12.130591	0.402027	-2.585534
C	10.943713	2.615955	-2.461657
C	10.082879	3.379762	-2.133701
C	8.961157	4.142016	-1.648516
C	8.783548	5.488777	-1.983619
C	7.675515	6.162836	-1.492876
H	7.553359	7.078233	-1.712572
C	6.741640	5.525408	-0.688205
C	6.913095	4.163854	-0.351779
C	8.025008	3.497688	-0.848080
H	8.149291	2.579966	-0.635266
C	9.341030	7.327915	-3.401322
C	10.386271	7.327655	-4.610974
H	11.290444	7.454932	-4.229815
H	10.368080	6.429183	-5.026545
C	10.207946	8.324282	-5.688280
H	9.290923	8.275836	-6.029736
H	10.836867	8.135326	-6.416190
H	10.378813	9.221320	-5.333590
C	6.141770	2.256263	0.853904
H	6.952308	2.190130	1.418761
H	6.263535	1.672644	0.063527
C	4.941216	1.813955	1.635017
H	4.142958	1.837257	1.050836
H	4.789332	2.441356	2.384896

C	5.120536	0.417921	2.178963
H	5.304741	-0.198877	1.439937
H	4.299983	0.142198	2.639002
H	5.869177	0.403062	2.811053
C	5.607615	6.249809	-0.193227
C	10.876862	0.616289	-0.397041
C	10.358608	1.123263	0.556387
C	9.855434	1.798165	1.713101
C	9.937864	3.186677	1.803627
H	10.253513	3.683617	1.058777
C	9.569668	3.854873	2.960870
C	9.139376	3.118361	4.073910
C	8.999472	1.723689	3.964856
H	8.671139	1.226870	4.703617
C	9.334229	1.064507	2.791731
C	9.870154	5.995986	1.914798
H	9.188991	5.781491	1.228181
H	10.762985	5.775695	1.548462
C	9.805462	7.456311	2.258901
H	10.533071	7.679846	2.890462
H	8.941916	7.653100	2.702529
C	9.938717	8.310238	1.010867
H	10.767053	8.075816	0.542623
H	9.963509	9.255957	1.265239
H	9.172638	8.150617	0.420864
C	8.762825	-1.080929	3.699897
H	7.898027	-0.742998	4.041882
H	9.423035	-1.070370	4.436276
C	8.602851	-2.513999	3.128686
H	8.480414	-3.114280	3.904241
H	7.746951	-2.522342	2.628414
C	9.430373	-3.049794	2.403424
H	9.749978	-2.406664	1.736395
H	9.030210	-3.821045	1.950797
H	10.182855	-3.350824	2.953988
C	8.846398	3.733807	5.337560
C	8.611590	4.121439	6.445306
C	8.267905	4.538863	7.783865
C	9.037530	5.496223	8.440836
C	8.660673	5.911720	9.726192
H	9.168608	6.573397	10.180142
C	7.561391	5.363682	10.319372
H	7.316772	5.648988	11.191274
C	6.791129	4.403209	9.686752
C	7.166934	3.976629	8.414896
H	6.667052	3.296474	7.977886

C	10.739851	7.174061	8.141996
H	10.889635	7.221379	9.118718
H	11.614744	7.282168	7.689369
C	9.865413	8.217490	7.742308
H	10.317857	9.084255	7.890537
H	9.062537	8.195875	8.319341
C	9.403111	8.143754	6.241491
H	10.193327	8.202229	5.664458
H	8.798054	8.888287	6.042971
H	8.941312	7.295216	6.077381
C	4.803632	3.088207	9.714280
H	5.246941	2.237966	9.468115
H	4.471603	3.517998	8.885787
C	3.646767	2.825968	10.675121
C	4.238803	2.015219	11.980063
H	4.693150	1.203662	11.670371
H	3.502699	1.766827	12.580920
H	4.876070	2.581516	12.464454
O	9.721560	6.071051	-2.777702
O	5.954357	3.610719	0.430393
O	9.626624	5.222774	3.107511
O	9.219998	-0.282108	2.600621
O	10.175167	5.911764	7.801070
O	5.712661	3.939568	10.374163
C	-1.611840	11.431298	3.042396
C	-2.264009	10.959024	4.173700
H	-2.142687	10.055266	4.438923
C	-3.104295	11.798501	4.934166
H	-3.545301	11.464821	5.706809
C	-3.272201	13.076645	4.555124
H	-3.825273	13.640161	5.084777
C	-2.654488	13.618596	3.390734
C	-2.844327	14.957304	3.022809
H	-3.381906	15.516511	3.570726
C	-2.281777	15.477296	1.906858
H	-2.413022	16.392317	1.688750
C	-1.499509	14.649847	1.067512
H	-1.119017	15.011844	0.275282
C	-1.279315	13.314856	1.386204
C	-1.822683	12.762029	2.585534
C	-0.635806	10.548101	2.461657
C	0.225029	9.784294	2.133701
C	1.346751	9.022040	1.648516
C	1.524360	7.675279	1.983619
C	2.632393	7.001219	1.492876
H	2.754549	6.085823	1.712572

C	3.566268	7.638647	0.688205
C	3.394813	9.000201	0.351779
C	2.282900	9.666368	0.848080
H	2.158617	10.584089	0.635266
C	0.966878	5.836141	3.401322
C	-0.078363	5.836401	4.610974
H	-0.982536	5.709123	4.229815
H	-0.060172	6.734873	5.026545
C	0.099962	4.839774	5.688280
H	1.016985	4.888220	6.029736
H	-0.528960	5.028730	6.416190
H	-0.070905	3.942736	5.333590
C	4.166138	10.907793	-0.853904
H	3.355599	10.973926	-1.418761
H	4.044373	11.491412	-0.063527
C	5.366692	11.350100	-1.635017
H	6.164950	11.326799	-1.050836
H	5.518576	10.722700	-2.384896
C	5.187371	12.746135	-2.178963
H	5.003167	13.362932	-1.439937
H	6.007925	13.021858	-2.639002
H	4.438731	12.760994	-2.811053
C	4.700293	6.914247	0.193227
C	-0.568954	12.547767	0.397041
C	-0.050700	12.040793	-0.556387
C	0.452474	11.365890	-1.713101
C	0.370044	9.977378	-1.803627
H	0.054395	9.480439	-1.058777
C	0.738240	9.309183	-2.960870
C	1.168532	10.045694	-4.073910
C	1.308436	11.440366	-3.964856
H	1.636769	11.937186	-4.703617
C	0.973679	12.099549	-2.791731
C	0.437754	7.168070	-1.914798
H	1.118917	7.382565	-1.228181
H	-0.455077	7.388361	-1.548462
C	0.502446	5.707745	-2.258901
H	-0.225163	5.484210	-2.890462
H	1.365991	5.510956	-2.702529
C	0.369190	4.853817	-1.010867
H	-0.459145	5.088240	-0.542623
H	0.344399	3.908099	-1.265239
H	1.135269	5.013439	-0.420864
C	1.545083	14.244984	-3.699897
H	2.409881	13.907054	-4.041882
H	0.884873	14.234426	-4.436276

C	1.705057	15.678055	-3.128686
H	1.827494	16.278336	-3.904241
H	2.560957	15.686398	-2.628414
C	0.877535	16.213850	-2.403424
H	0.557930	15.570720	-1.736395
H	1.277698	16.985101	-1.950797
H	0.125053	16.514880	-2.953988
C	1.461510	9.430249	-5.337560
C	1.696318	9.042617	-6.445306
C	2.040003	8.625193	-7.783865
C	1.270378	7.667833	-8.440836
C	1.647235	7.252336	-9.726192
H	1.139300	6.590658	-10.180142
C	2.746517	7.800374	-10.319372
H	2.991136	7.515068	-11.191274
C	3.516778	8.760847	-9.686752
C	3.140973	9.187427	-8.414896
H	3.640856	9.867582	-7.977886
C	-0.431943	5.989995	-8.141996
H	-0.581727	5.942676	-9.118718
H	-1.306836	5.881888	-7.689369
C	0.442495	4.946566	-7.742308
H	-0.009949	4.079800	-7.890537
H	1.245371	4.968181	-8.319341
C	0.904797	5.020302	-6.241491
H	0.114581	4.961827	-5.664458
H	1.509853	4.275769	-6.042971
H	1.366596	5.868840	-6.077381
C	5.504276	10.075849	-9.714280
H	5.060966	10.926089	-9.468115
H	5.836305	9.646058	-8.885787
C	6.661141	10.338088	-10.675121
C	6.069105	11.148837	-11.980063
H	5.614758	11.960394	-11.670371
H	6.805209	11.397229	-12.580920
H	5.431838	10.582540	-12.464454
O	0.586348	7.093005	2.777702
O	4.353551	9.553337	-0.430393
O	0.681283	7.941282	-3.107511
O	1.087910	13.446163	-2.600621
O	0.132741	7.252292	-7.801070
O	4.595247	9.224488	-10.374163
C	14.964068	-3.938172	10.805350
C	15.493859	-5.143999	11.229390
H	14.913023	-5.811360	11.575081
C	16.877289	-5.402641	11.159511

H	17.222286	-6.249737	11.418912
C	17.712061	-4.426700	10.716678
H	18.648268	-4.587624	10.706884
C	17.226565	-3.184096	10.270668
C	18.113882	-2.168259	9.859598
H	19.050407	-2.316959	9.920742
C	17.658474	-0.981791	9.378119
H	18.271110	-0.298419	9.131953
C	16.289413	-0.774479	9.247095
H	15.979995	0.041861	8.872553
C	15.366513	-1.727326	9.647842
C	15.811387	-2.947173	10.237316
C	13.558486	-3.724735	11.077985
C	12.419223	-3.673876	11.453851
C	11.058930	-3.552382	11.887420
C	10.406288	-4.609651	12.513158
C	9.081572	-4.482628	12.889818
H	8.645715	-5.213295	13.314123
C	8.373358	-3.303961	12.659004
C	9.034341	-2.221290	12.048355
C	10.366641	-2.351892	11.664548
H	10.809978	-1.622095	11.249507
C	10.797985	-6.595683	13.766750
C	12.003934	-7.408233	14.102912
C	12.891240	-8.107092	13.287653
C	8.943895	0.071574	11.341091
H	9.304947	-0.121172	10.439543
H	9.699626	0.321023	11.929772
C	7.972738	1.202422	11.262742
H	8.411502	1.960074	10.802174
H	7.205602	0.917584	10.706884
C	7.465311	1.673582	12.546509
H	8.185836	1.597756	13.208245
H	6.697694	1.140887	12.840320
H	7.199031	2.612417	12.461807
C	7.003031	-3.170768	13.065310
C	13.981715	-1.446334	9.332856
C	12.895139	-1.109421	8.953814
C	11.573238	-0.794143	8.493510
C	10.624202	-1.805915	8.329400
H	10.859156	-2.700441	8.544332
C	9.350101	-1.538725	7.860891
C	9.005209	-0.220790	7.536376
C	9.936045	0.789046	7.708692
H	9.695891	1.683010	7.496142
C	11.211905	0.523807	8.185671

C	8.620054	-3.796881	8.192288
H	8.763145	-3.762035	9.171657
H	9.436157	-4.169482	7.774071
C	7.427491	-4.681600	7.874655
H	6.607793	-4.265539	8.242580
H	7.321421	-4.744782	6.892639
C	7.578497	-6.045459	8.438454
H	8.375998	-6.470245	8.057294
H	6.787513	-6.581366	8.221405
H	7.676585	-5.985669	9.412529
C	11.814347	2.858798	8.186994
H	11.001367	3.081293	8.705795
H	11.630851	3.024315	7.228801
C	12.980065	3.709861	8.652856
H	13.203619	3.498692	9.592521
H	12.744414	4.670720	8.591977
C	14.208471	3.394535	7.718485
H	14.152172	2.460754	7.424675
H	15.041358	3.529253	8.218758
H	14.198664	3.983526	6.934990
C	7.694110	0.110370	7.031074
C	6.643495	0.449472	6.575800
C	5.404354	0.930620	6.048529
C	4.297202	0.053516	5.905065
C	3.106406	0.573691	5.418821
H	2.344649	0.012016	5.338884
C	3.019030	1.866018	5.057778
H	2.194662	2.192622	4.716852
C	4.093423	2.740397	5.168156
C	5.298786	2.255895	5.659429
H	6.050406	2.832103	5.727984
C	3.443374	-2.171592	5.968062
H	3.148157	-2.092943	5.026545
H	2.669160	-1.992475	6.559124
C	4.003347	-3.562484	6.233550
H	4.337121	-3.611178	7.165274
H	3.281752	-4.233815	6.132967
C	5.115566	-3.885775	5.293886
H	5.464647	-4.774843	5.513582
H	5.833697	-3.223929	5.373294
H	4.771877	-3.887595	4.375397
C	4.983898	4.916854	4.814789
H	4.784825	5.558653	5.542698
H	5.779511	4.400513	5.100659
C	5.289936	5.518910	3.920122
H	4.461358	5.922413	3.560138

H	5.604507	4.870511	3.242505
C	6.314185	6.621837	3.954533
H	5.862040	7.489367	3.904241
H	6.927189	6.525318	3.197507
H	6.819274	6.564724	4.793614
O	11.100154	-5.784904	12.707179
O	8.293979	-1.087346	11.856451
O	8.369857	-2.484432	7.690163
O	12.171884	1.483025	8.393985
O	4.505935	-1.241531	6.238580
O	3.905225	4.011242	4.758674
C	-2.100689	-2.306903	15.664079
C	-2.630481	-1.101076	15.240038
H	-2.049644	-0.433715	14.894348
C	-4.013910	-0.842434	15.309918
H	-4.358907	0.004662	15.050517
C	-4.848683	-1.818375	15.752751
H	-5.784889	-1.657451	15.762545
C	-4.363186	-3.060979	16.198761
C	-5.250503	-4.076816	16.609831
H	-6.187028	-3.928116	16.548687
C	-4.795095	-5.263284	17.091310
H	-5.407731	-5.946656	17.337476
C	-3.426034	-5.470596	17.222334
H	-3.116616	-6.286936	17.596876
C	-2.503134	-4.517749	16.821587
C	-2.948008	-3.297902	16.232113
C	-0.695107	-2.520340	15.391443
C	0.444156	-2.571199	15.015578
C	1.804449	-2.692693	14.582008
C	2.457091	-1.635424	13.956271
C	3.781807	-1.762447	13.579611
H	4.217664	-1.031780	13.155306
C	4.490021	-2.941114	13.810424
C	3.829038	-4.023785	14.421074
C	2.496738	-3.893183	14.804881
H	2.053401	-4.622980	15.219922
C	2.065394	0.350608	12.702679
C	0.859445	1.163158	12.366517
C	-0.027861	1.862016	13.181776
C	3.919484	-6.316649	15.128337
H	3.558432	-6.123903	16.029886
H	3.163753	-6.566098	14.539657
C	4.890641	-7.447497	15.206687
H	4.451877	-8.205149	15.667255
H	5.657777	-7.162659	15.762545

C	5.398068	-7.918657	13.922920
H	4.677543	-7.842831	13.261184
H	6.165685	-7.385962	13.629109
H	5.664348	-8.857492	14.007622
C	5.860348	-3.074307	13.404119
C	-1.118336	-4.798741	17.136573
C	-0.031760	-5.135655	17.515615
C	1.290141	-5.450932	17.975918
C	2.239177	-4.439160	18.140029
H	2.004223	-3.544634	17.925097
C	3.513278	-4.706350	18.608538
C	3.858170	-6.024285	18.933053
C	2.927334	-7.034121	18.760737
H	3.167488	-7.928085	18.973287
C	1.651474	-6.768882	18.283758
C	4.243325	-2.448194	18.277141
H	4.100234	-2.483040	17.297772
H	3.427222	-2.075593	18.695358
C	5.435888	-1.563475	18.594774
H	6.255586	-1.979536	18.226849
H	5.541958	-1.500293	19.576790
C	5.284882	-0.199616	18.030975
H	4.487381	0.225170	18.412135
H	6.075866	0.336291	18.248024
H	5.186794	-0.259406	17.056900
C	1.049032	-9.103873	18.282434
H	1.862012	-9.326368	17.763634
H	1.232528	-9.269390	19.240628
C	-0.116686	-9.954936	17.816573
H	-0.340240	-9.743767	16.876908
H	0.118965	-10.915795	17.877452
C	-1.345092	-9.639610	18.750943
H	-1.288793	-8.705829	19.044754
H	-2.177979	-9.774328	18.250671
H	-1.335285	-10.228601	19.534438
C	5.169269	-6.355445	19.438354
C	6.219884	-6.694548	19.893629
C	7.459025	-7.175695	20.420900
C	8.566177	-6.298591	20.564364
C	9.756973	-6.818766	21.050607
H	10.518730	-6.257091	21.130545
C	9.844349	-8.111093	21.411650
H	10.668717	-8.437697	21.752577
C	8.769956	-8.985472	21.301273
C	7.564593	-8.500970	20.810000
H	6.812973	-9.077178	20.741444

C	9.420005	-4.073483	20.501367
H	9.715222	-4.152132	21.442884
H	10.194219	-4.252600	19.910304
C	8.860032	-2.682591	20.235878
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C	7.747813	-2.359300	21.175543
H	7.398732	-1.470232	20.955847
H	7.029682	-3.021146	21.096135
H	8.091502	-2.357480	22.094032
C	7.879481	-11.161929	21.654640
H	8.078554	-11.803728	20.926730
H	7.083868	-10.645588	21.368770
C	7.573443	-11.763985	22.549306
H	8.402021	-12.167488	22.909291
H	7.258872	-11.115586	23.226924
C	6.549194	-12.866912	22.514896
H	7.001339	-13.734442	22.565188
H	5.936190	-12.770393	23.271922
H	6.044105	-12.809799	21.675815
O	1.763225	-0.460171	13.762250
O	4.569400	-5.157729	14.612978
O	4.493522	-3.760643	18.779266
O	0.691495	-7.728100	18.075444
O	8.357444	-5.003544	20.230849
O	8.958154	-10.256317	21.710755
C	10.385516	7.926084	-4.084233
H	11.161844	8.051551	-3.483377
H	10.108230	8.812286	-4.425688
C	10.731446	7.071221	-5.158892
H	10.973896	6.188411	-4.809495
H	11.492150	7.450728	-5.645929
H	9.966104	6.982546	-5.765042
C	2.977806	4.330449	10.765117
H	3.612256	4.935007	11.204509
H	2.153035	4.282523	11.291858
H	2.774340	4.668532	9.867803
C	11.936404	-5.906866	13.793219
C	12.508741	-7.315132	13.764103
C	13.092064	-7.396983	14.417898

Table A3. Crystallographic data for **1,8-(4-Propyloxyphenylethynyl)naphthalene, IV-3**.

Total Number of Atomic Coordinates: 62

Atom	X	Y	Z
C	-0.933795	5.105165	7.391751
C	-0.933795	3.694945	7.391751
C	0.236739	2.968973	7.083268
H	0.205969	2.021038	7.054687
C	1.408521	3.613169	6.824064
H	2.201129	3.115836	6.655532
C	1.435925	5.008369	6.808295
H	2.260172	5.443952	6.625965
C	0.315961	5.786076	7.047788
C	0.443143	7.192959	7.046802
C	0.674712	8.377878	7.035961
C	0.832161	9.798112	6.984712
C	0.568773	10.602522	8.123041
H	0.332520	10.176952	8.940076
C	0.642140	11.947655	8.086575
H	0.475643	12.455001	8.872072
C	0.966437	12.605202	6.868415
C	1.210019	11.830832	5.721215
H	1.436306	12.251395	4.900238
C	1.123325	10.479023	5.792176
H	1.263538	9.971678	5.001751
C	1.325616	14.634584	5.705446
H	0.634976	14.454343	5.019491
H	2.197063	14.310818	5.362469
C	1.400996	16.123243	5.984361
H	0.529674	16.431989	6.338180
H	2.087525	16.290133	6.679186
C	1.735259	16.895944	4.781970
H	1.758068	17.850554	5.003722
H	1.057075	16.737398	4.092073
H	2.613059	16.617237	4.447863
O	0.998453	13.960349	6.910794
C	-2.104329	2.968973	7.700233
H	-2.073560	2.021038	7.728814
C	-3.276112	3.613169	7.959437
H	-4.068719	3.115836	8.127969
C	-3.303516	5.008369	7.975206
H	-4.127762	5.443952	8.157536
C	-2.183551	5.786076	7.735713
C	-2.310734	7.192959	7.736699
C	-2.542303	8.377878	7.747540

C	-2.699752	9.798112	7.798790
C	-2.436363	10.602522	6.660460
H	-2.200111	10.176952	5.843425
C	-2.509731	11.947655	6.696926
H	-2.343234	12.455001	5.911429
C	-2.834028	12.605202	7.915087
C	-3.077609	11.830832	9.062286
H	-3.303897	12.251395	9.883263
C	-2.990915	10.479023	8.991325
H	-3.131129	9.971678	9.781750
C	-3.193206	14.634584	9.078055
H	-2.502566	14.454343	9.764010
H	-4.064654	14.310818	9.421033
C	-3.268586	16.123243	8.799140
H	-2.397264	16.431989	8.445321
H	-3.955116	16.290133	8.104315
C	-3.602849	16.895944	10.001531
H	-3.625659	17.850554	9.779779
H	-2.924666	16.737398	10.691428
H	-4.480650	16.617237	10.335638
O	-2.866044	13.960349	7.872707

APPENDIX B

^{1}HNMR, ^{13}CNMR, AND IR SPECTRA FOR REPORTED COMPOUNDS

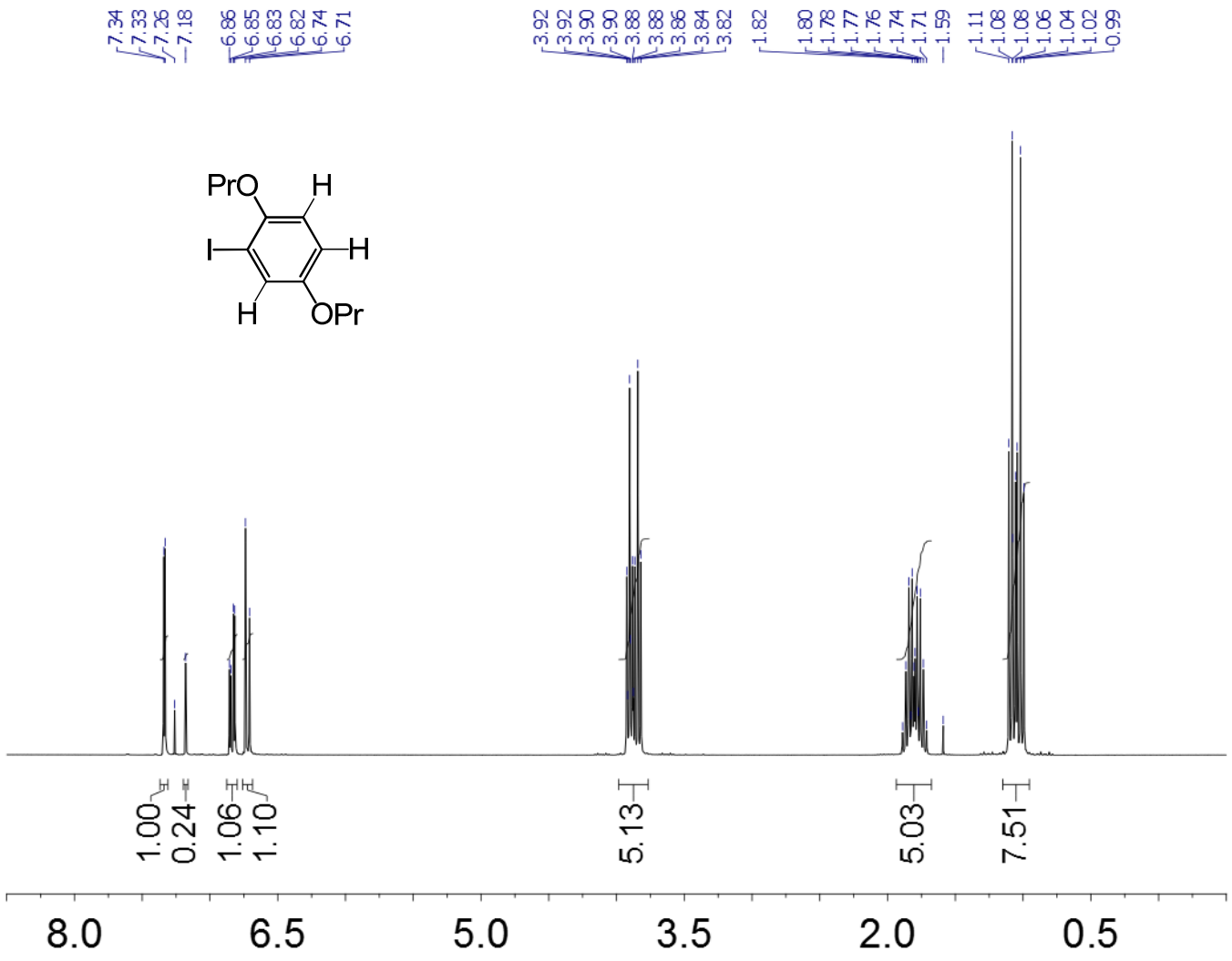

Figure B1. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1-Iodo-2,5-dipropyloxybenzene, II-1a**.

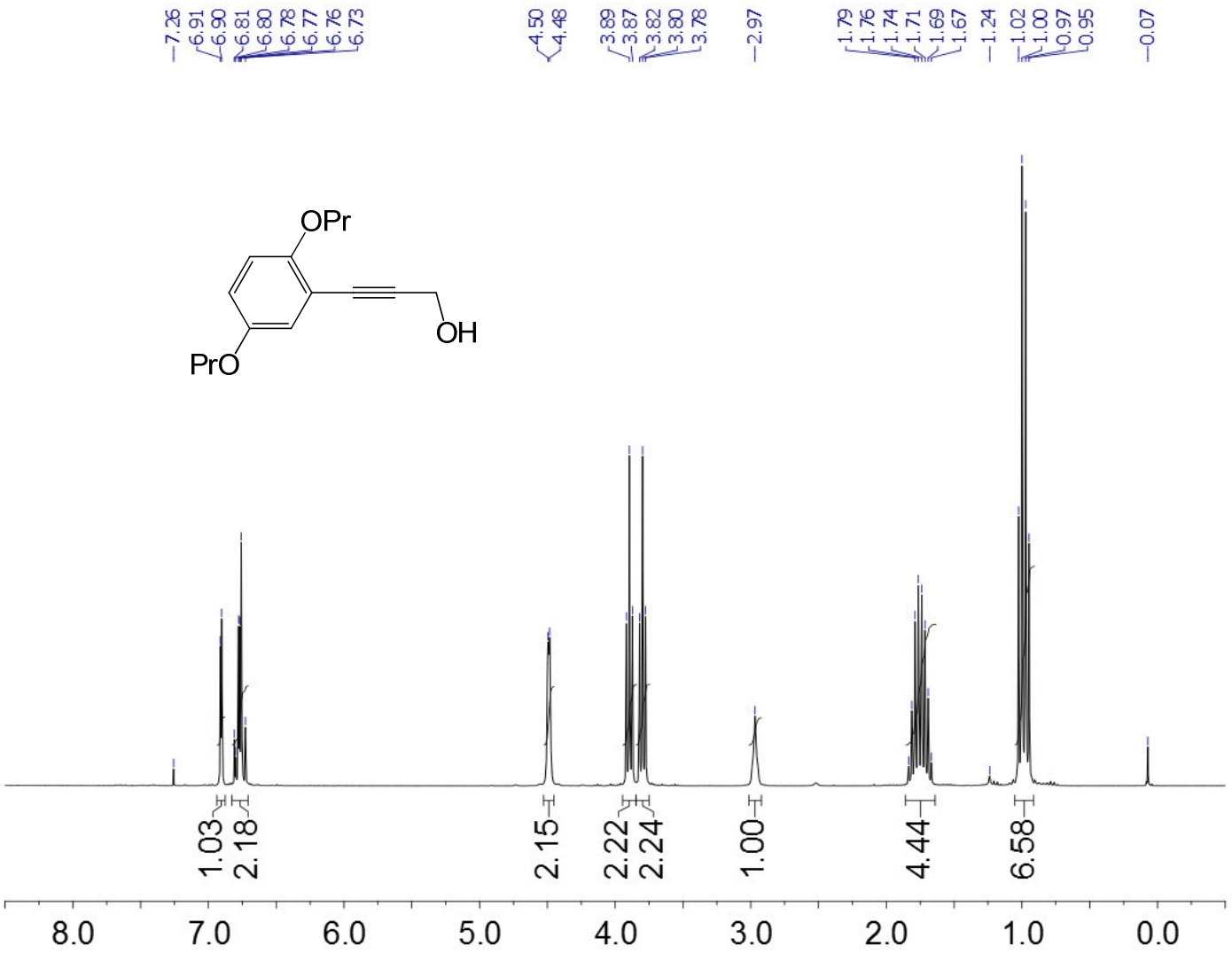

Figure B2. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1-(2,5-Dipropoxyphenyl)propyn-3-ol, II-1b**.

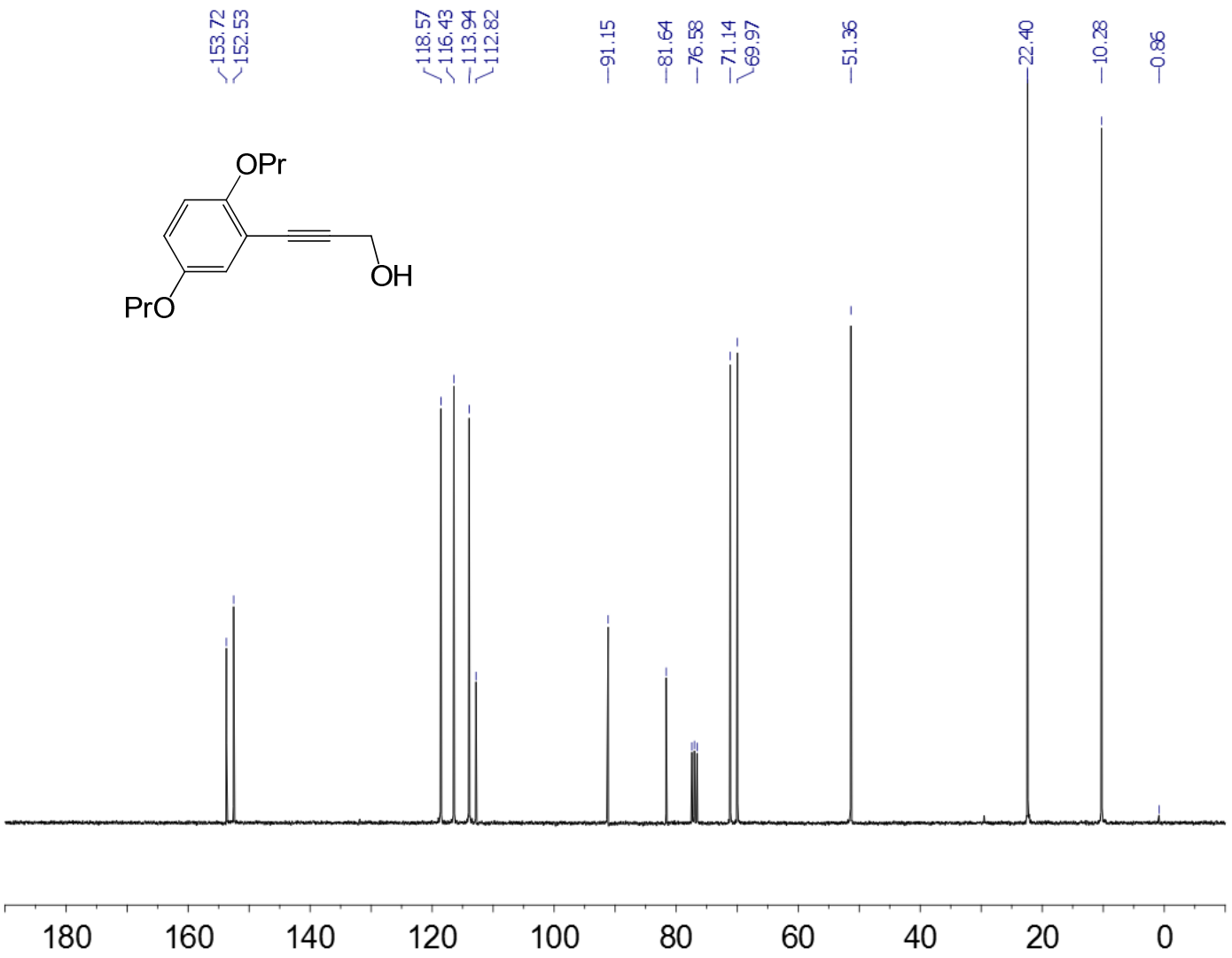

Figure B3. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1-(2,5-Dipropoxyphenyl)propyn-3-ol, II-1b**.

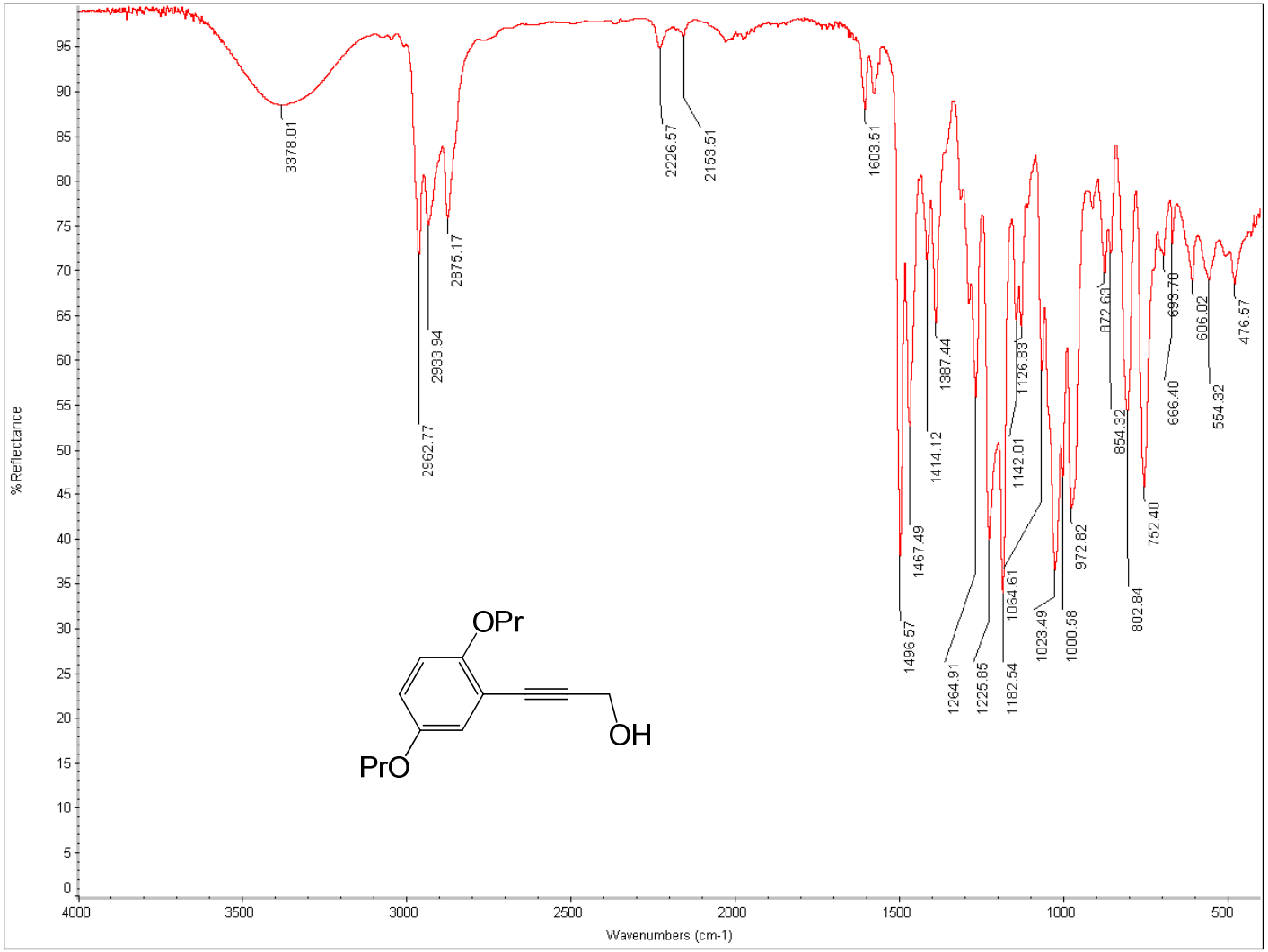

Figure B4. IR (ATIR, neat film) of **1-(2,5-Dipropoxyphenyl)propyn-3-ol, II-1b**.

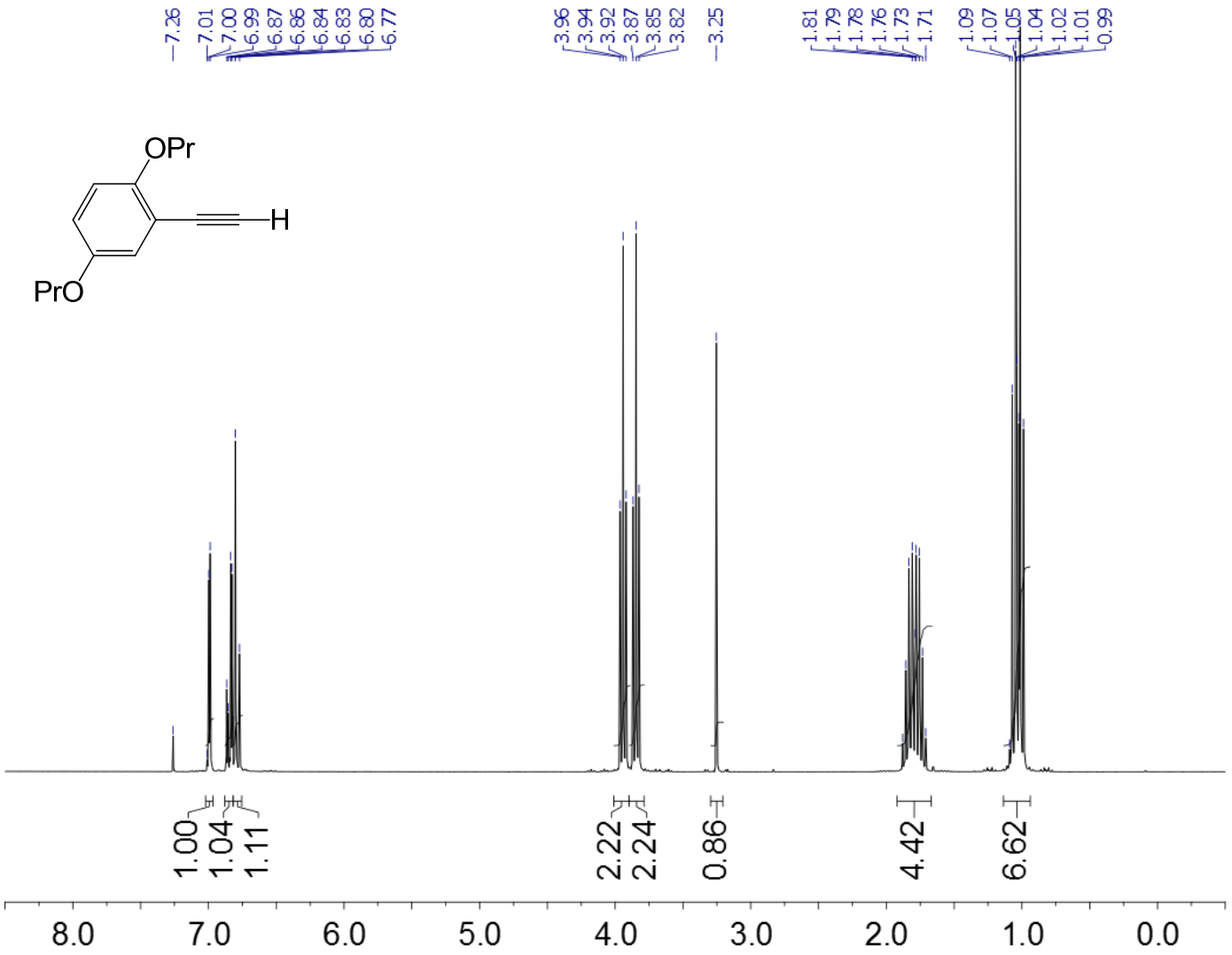

Figure B5. ^{1}HNMR ($CDCl_3$, 300 MHz) of **2-Ethynyl-1,4-dipropyloxybenzene, II-2**.

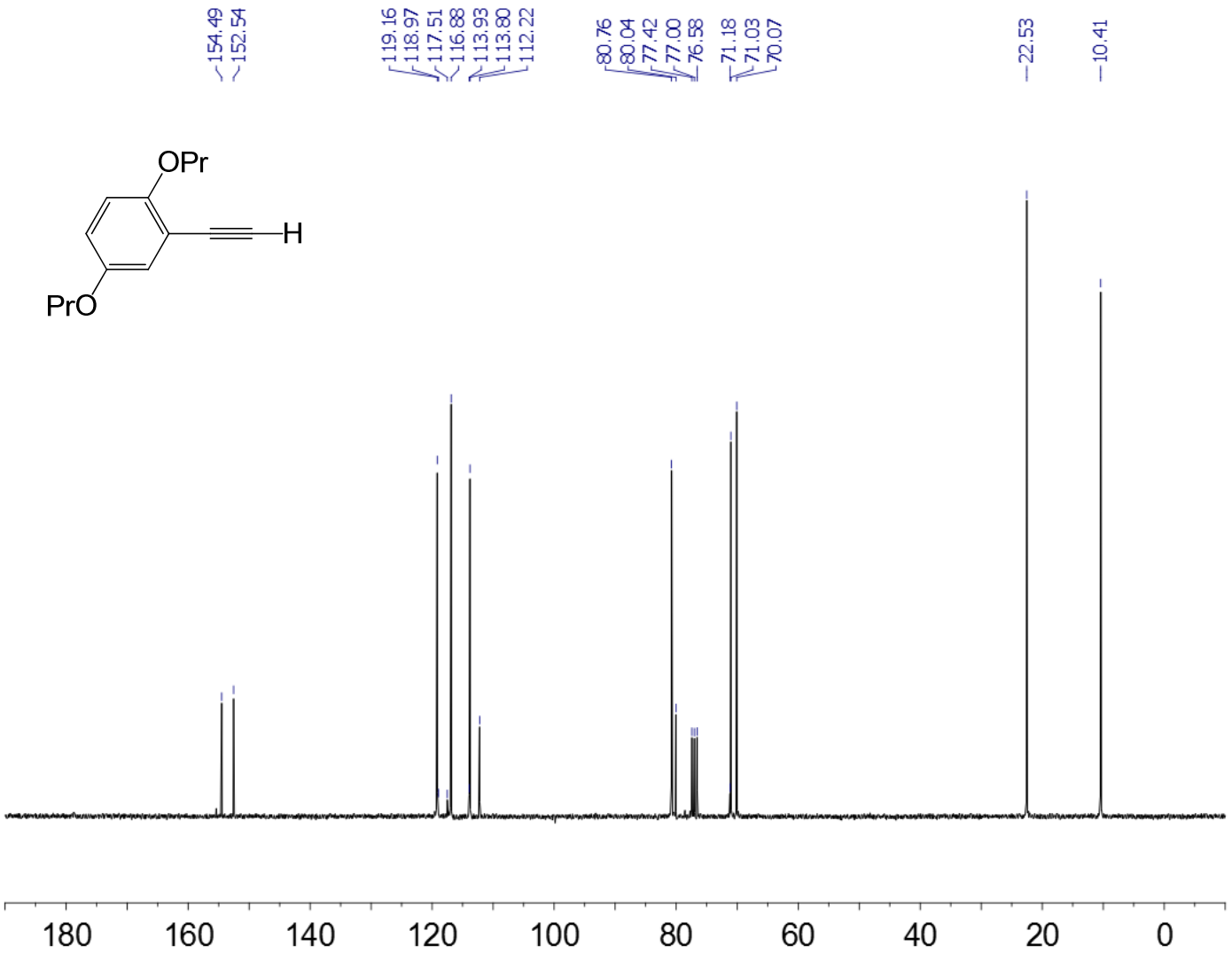

Figure B6. ^{13}CNMR ($CDCl_3$, 300 MHz) of **2-Ethynyl-1,4-dipropyloxybenzene, II-2**.

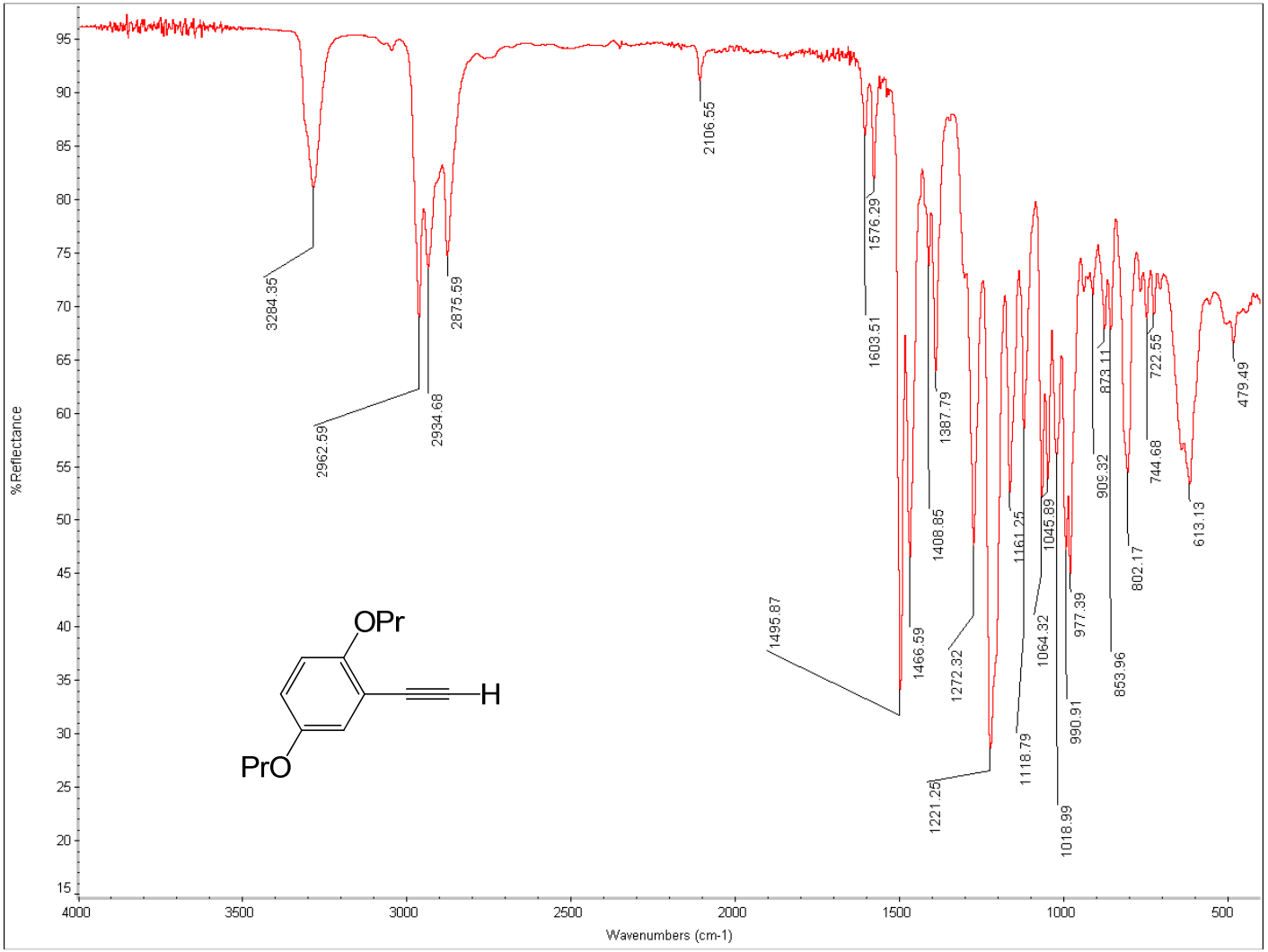

Figure B7. IR (ATIR, neat film) of **2-Ethynyl-1,4-dipropyloxybenzene, II-2**.

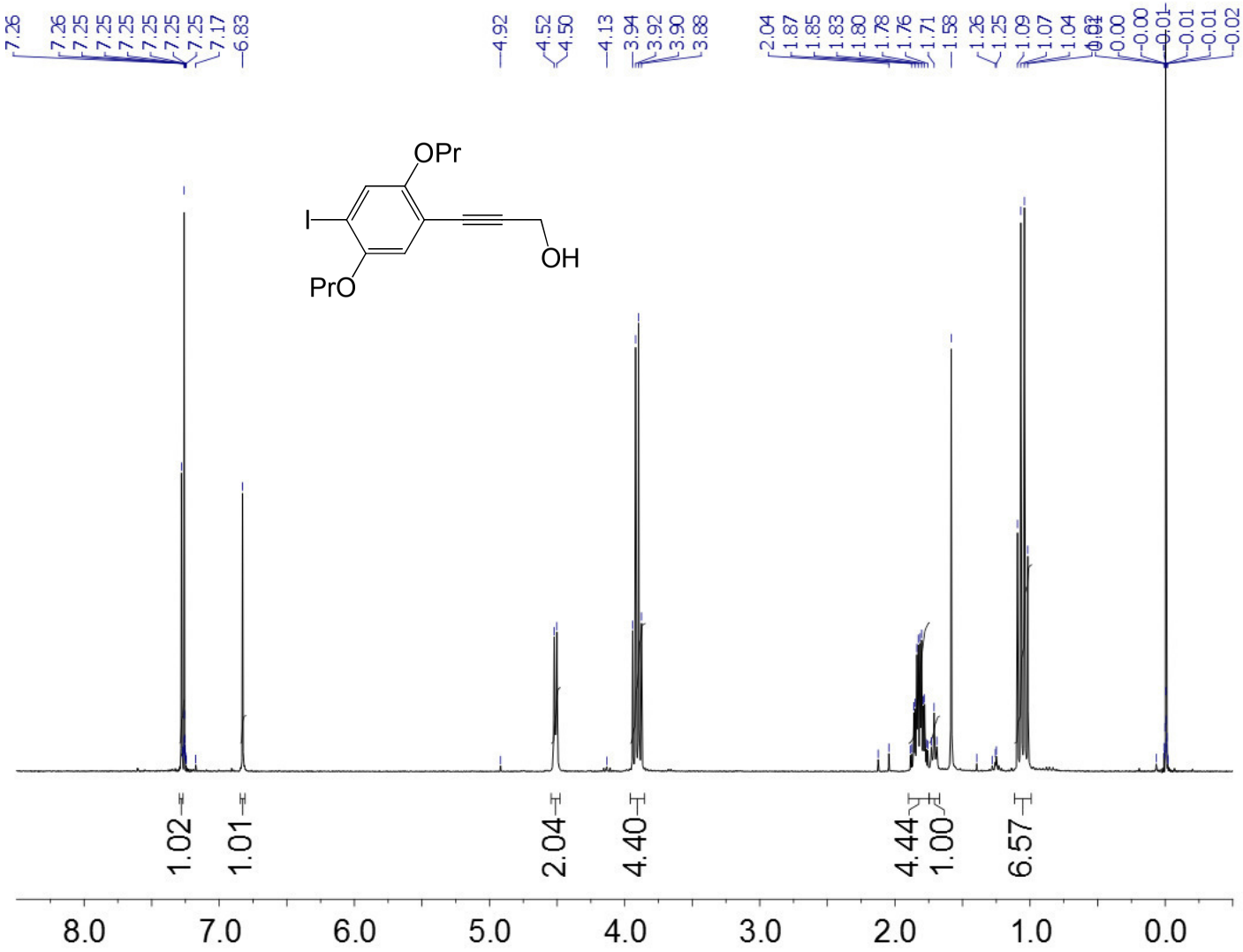

Figure B8. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1-(4-Iodo-2,5-dimethoxyphenyl)propyn-3-ol, II-3**.

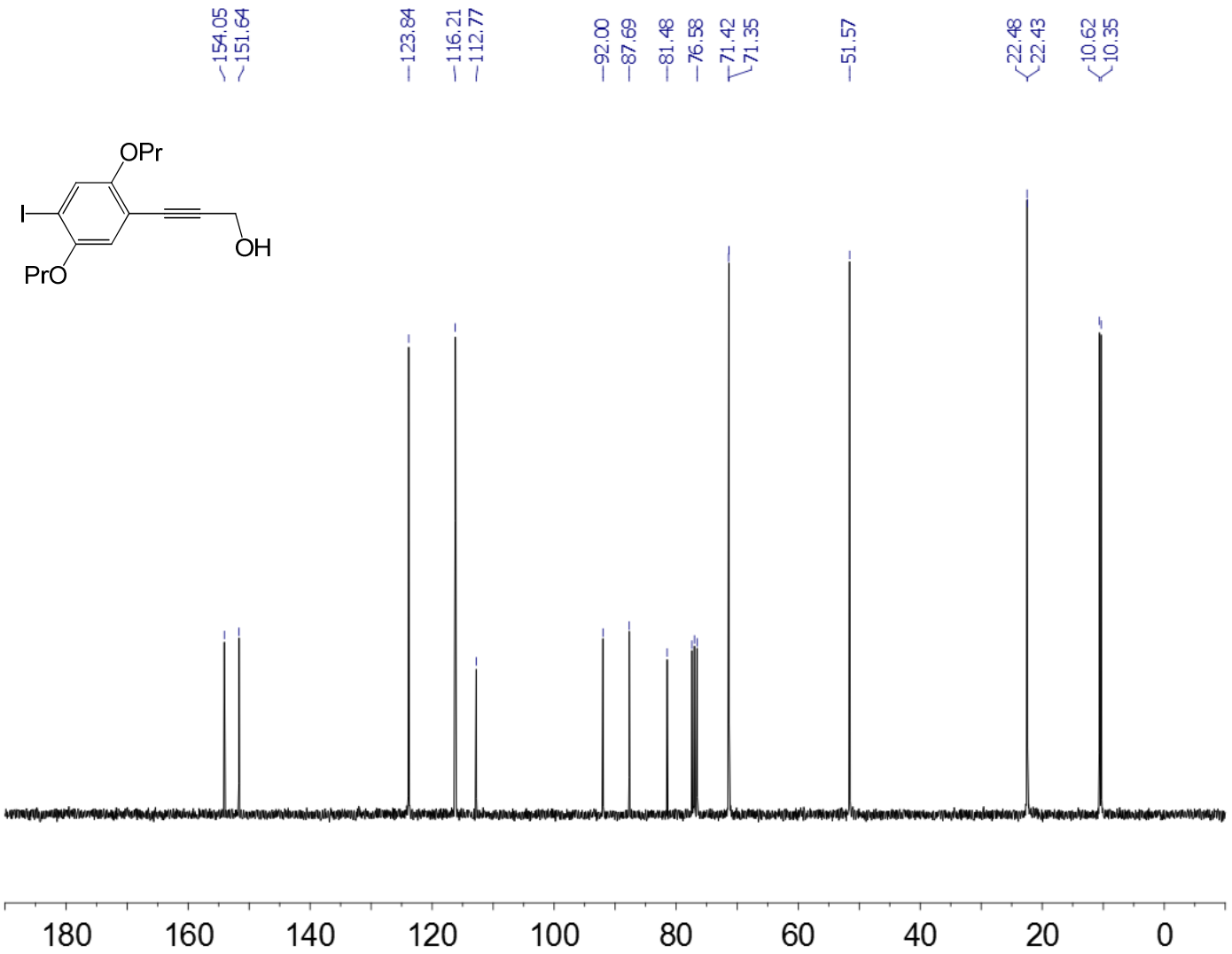

Figure B9. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1-(4-Iodo-2,5-dimethoxyphenyl)propyn-3-ol, II-3**.

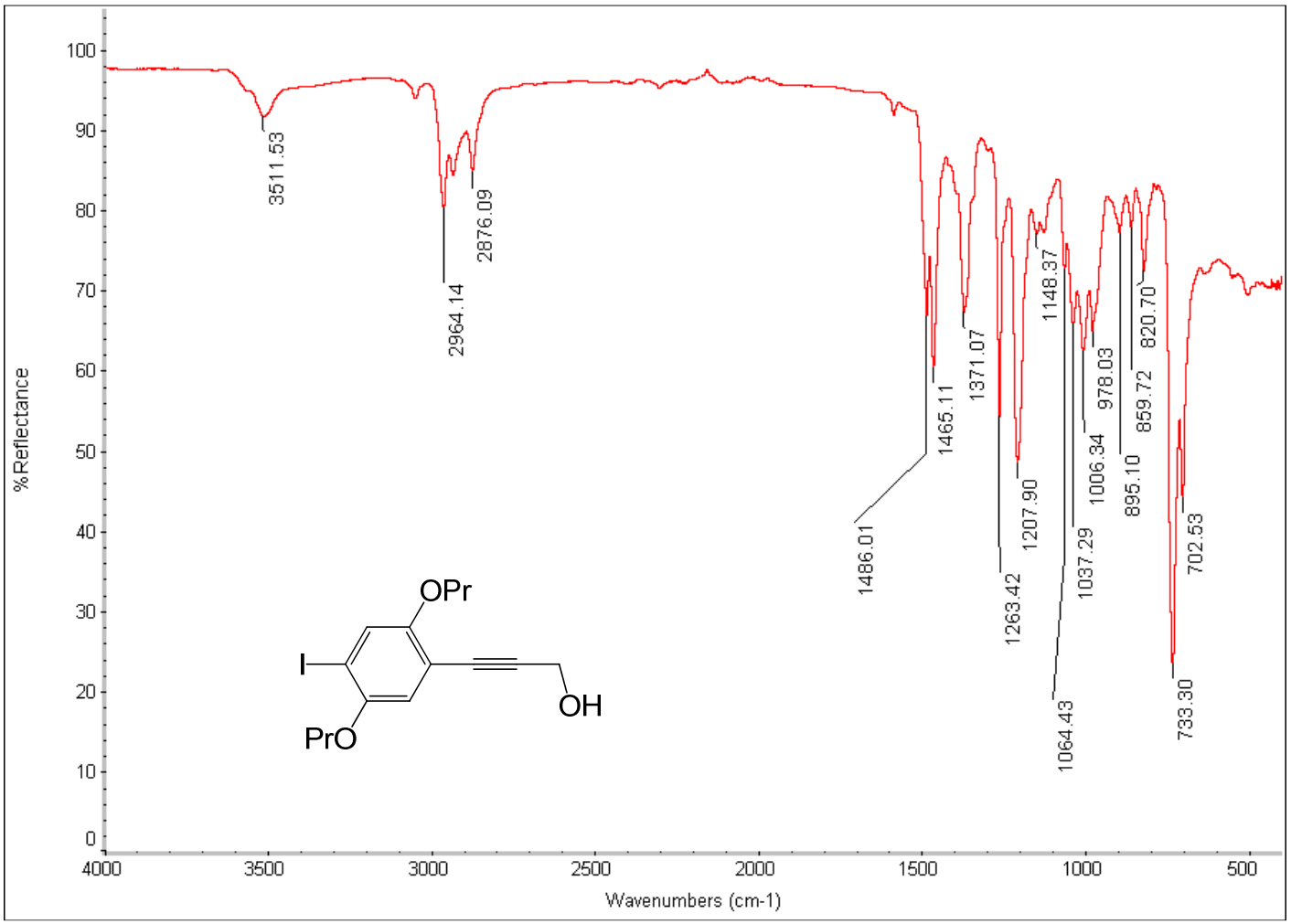

Figure B10. IR (ATIR, neat) of **1-(4-Iodo-2,5-dimethoxyphenyl)propyn-3-ol, II-3**.

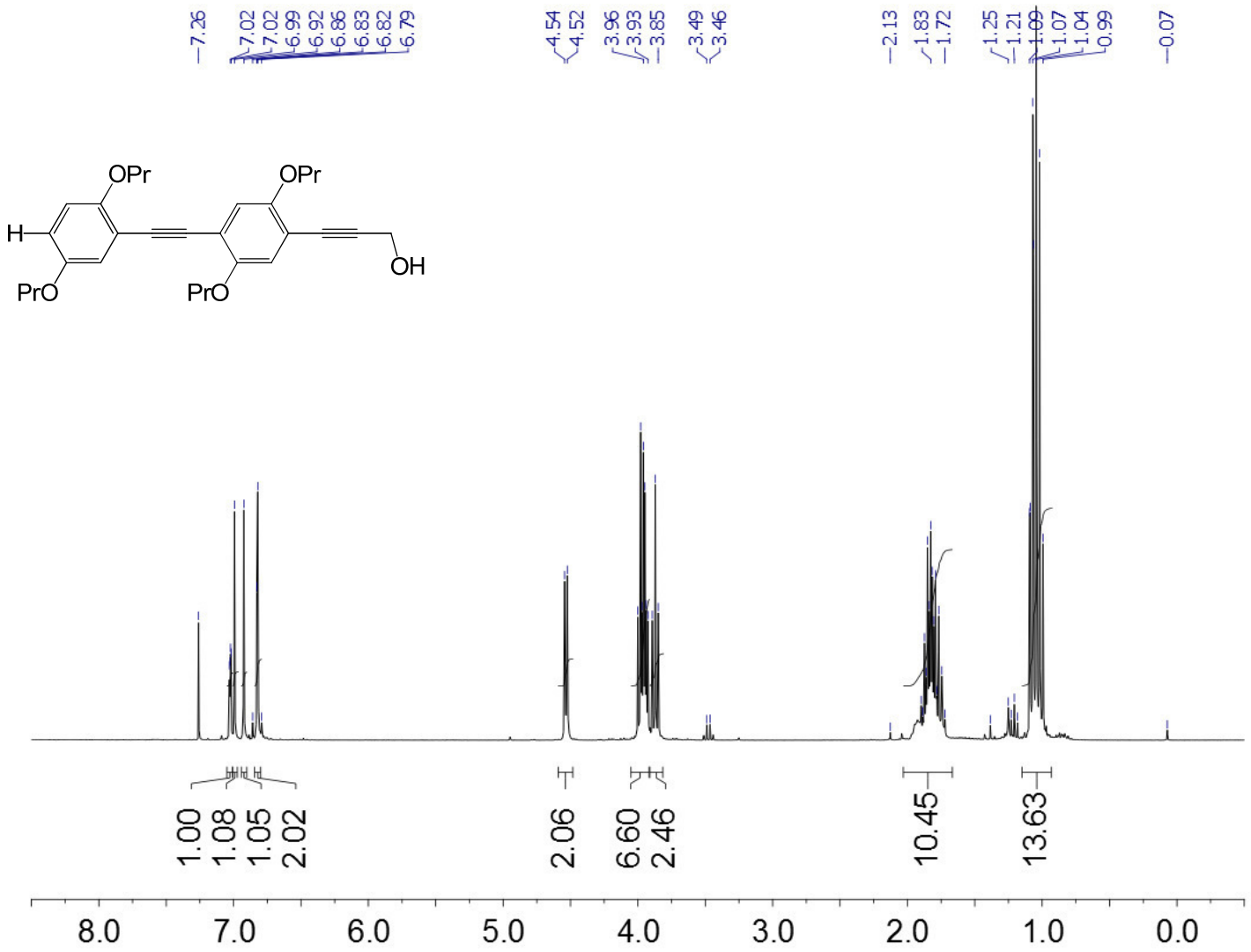

Figure B11. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropoxyphenyl)propyn-3-ol, II-4**.

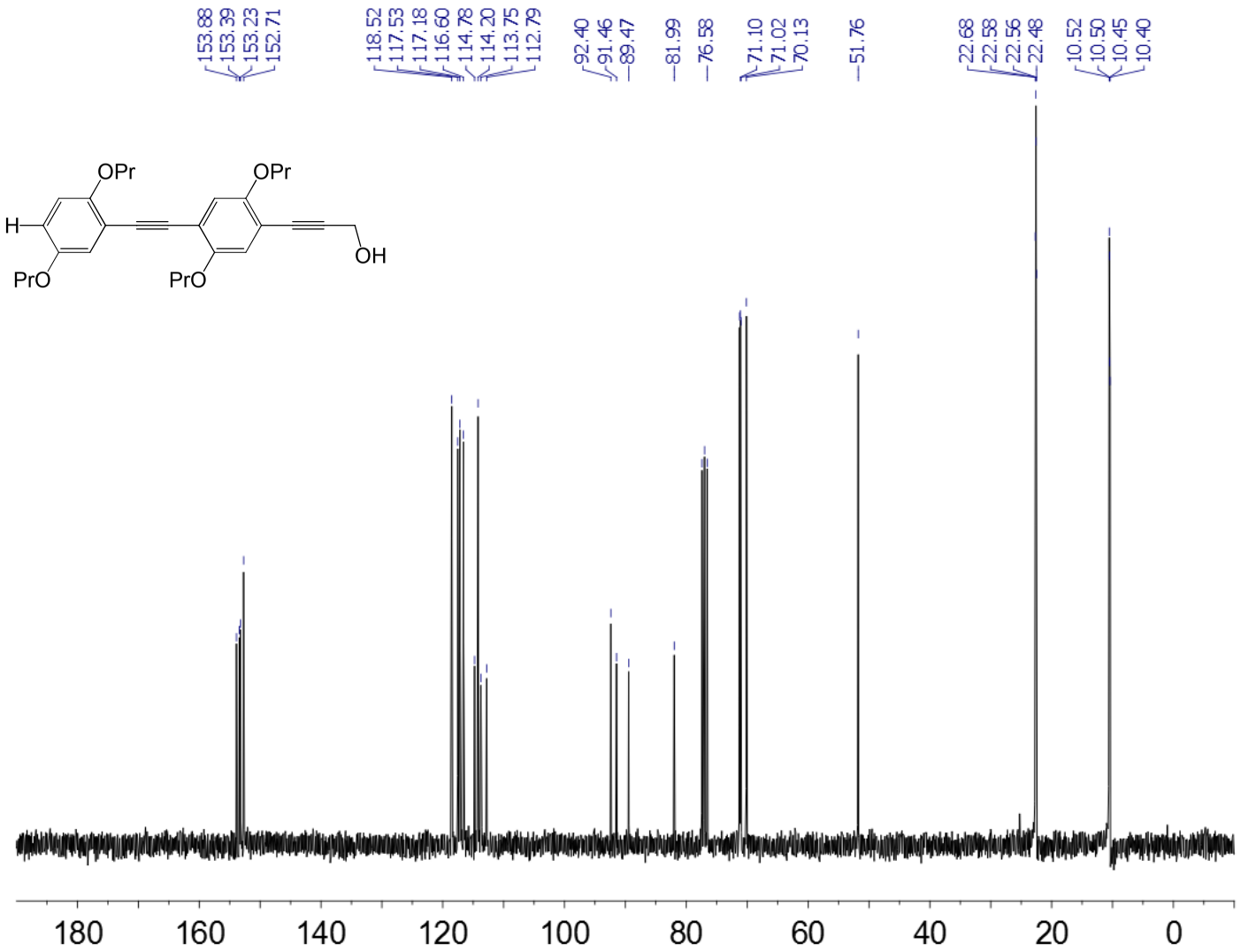

Figure B12. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropoxyphenyl)propyn-3-ol, II-4**.

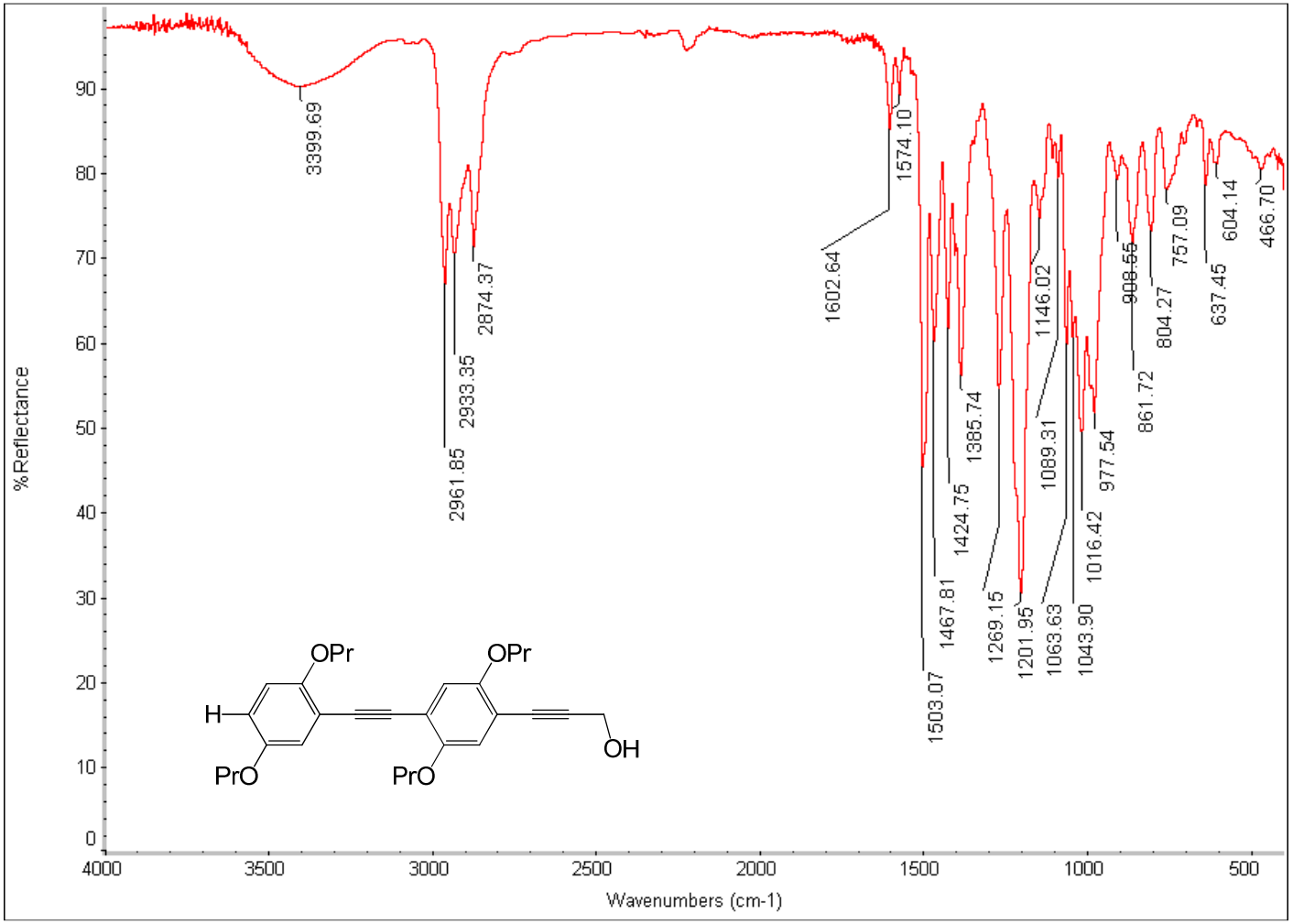

Figure B13. IR (ATIR, neat) of **1-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropoxyphenyl)propyn-3-ol, II-4**.

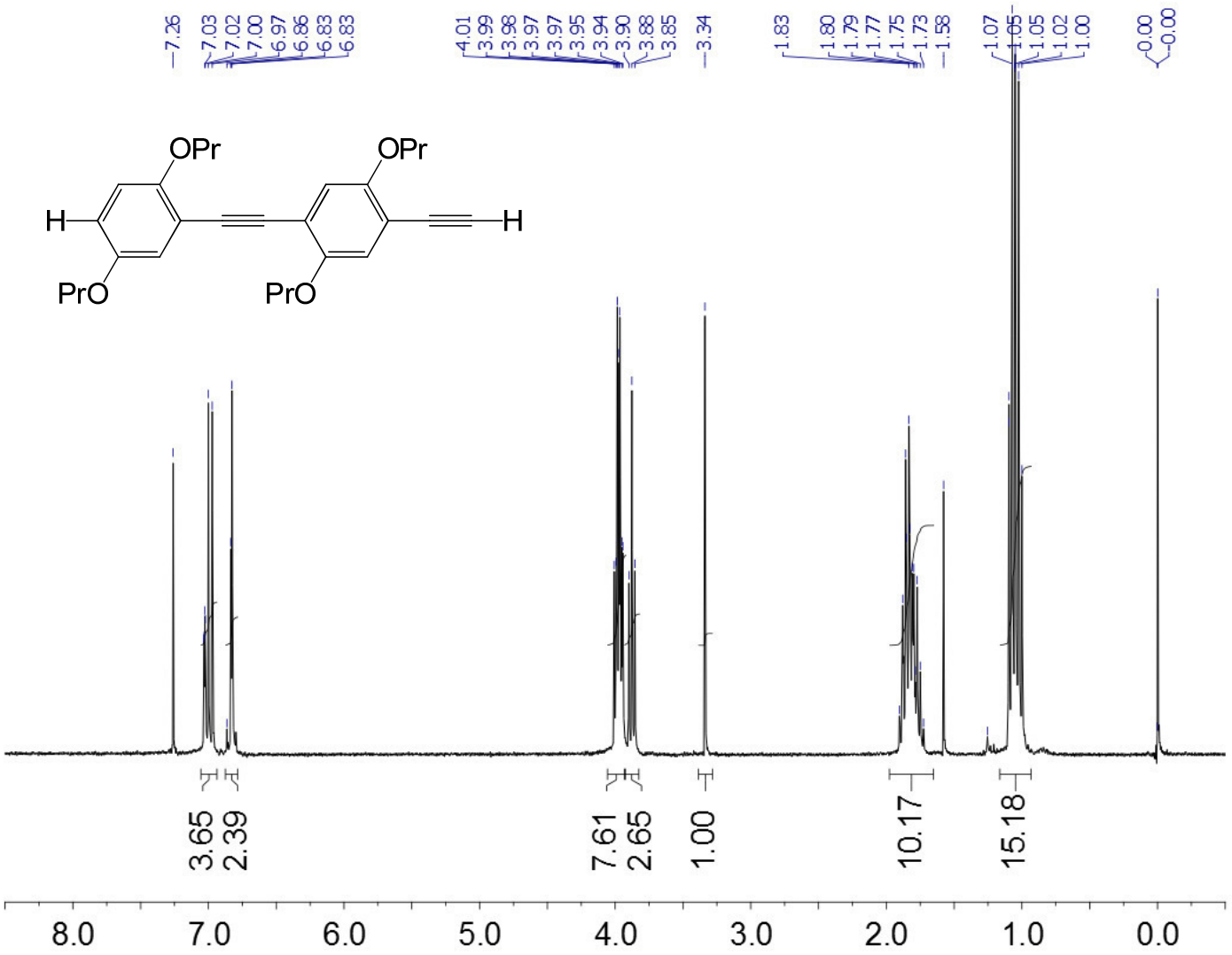

Figure B14. ^{1}HNMR ($CDCl_3$, 300 MHz) of **(4-(2,5-Dipropyloxyphenylethynyl)-2,5-di-propyloxyphenyl)acetylene, II-5**.

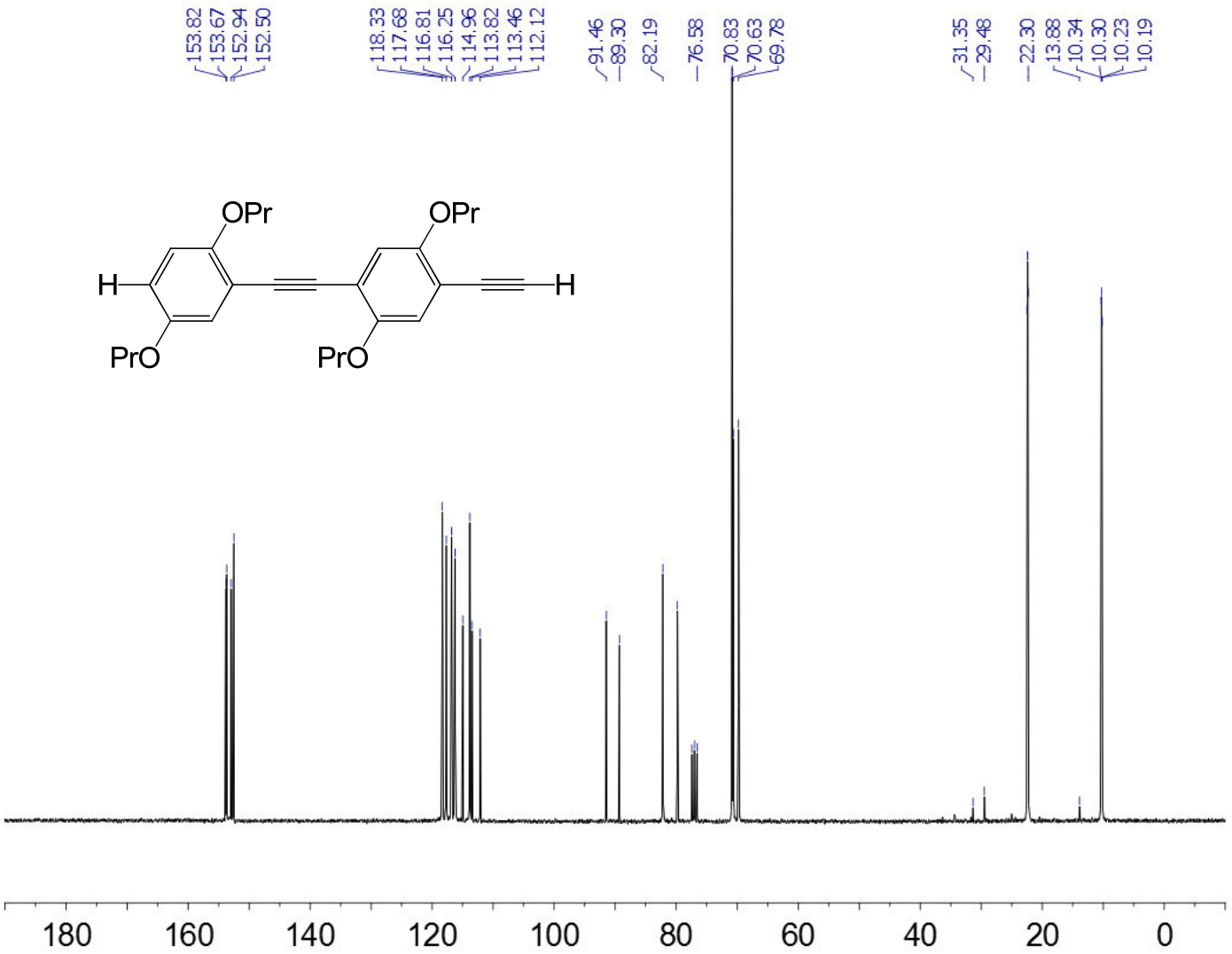

Figure B15. ^{13}CNMR ($CDCl_3$, 300 MHz) of **(4-(2,5-Dipropyloxyphenylethynyl)-2,5-di-propyloxyphenyl)acetylene, II-5**.

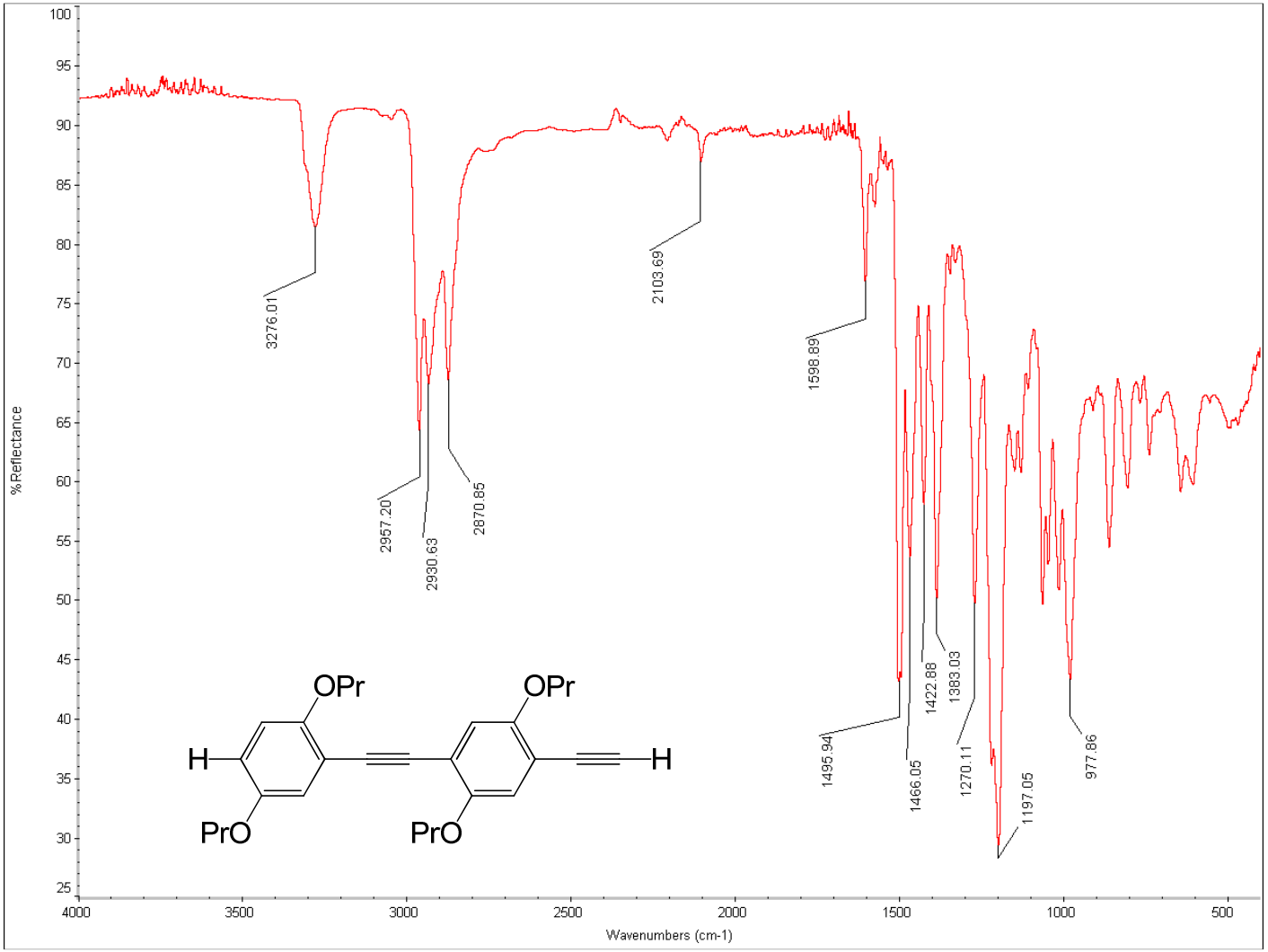

Figure B16. IR (ATIR, neat) of **(4-(2,5-Dipropyloxyphenylethynyl)-2,5-di-propyloxyphenyl)acetylene, II-5**.

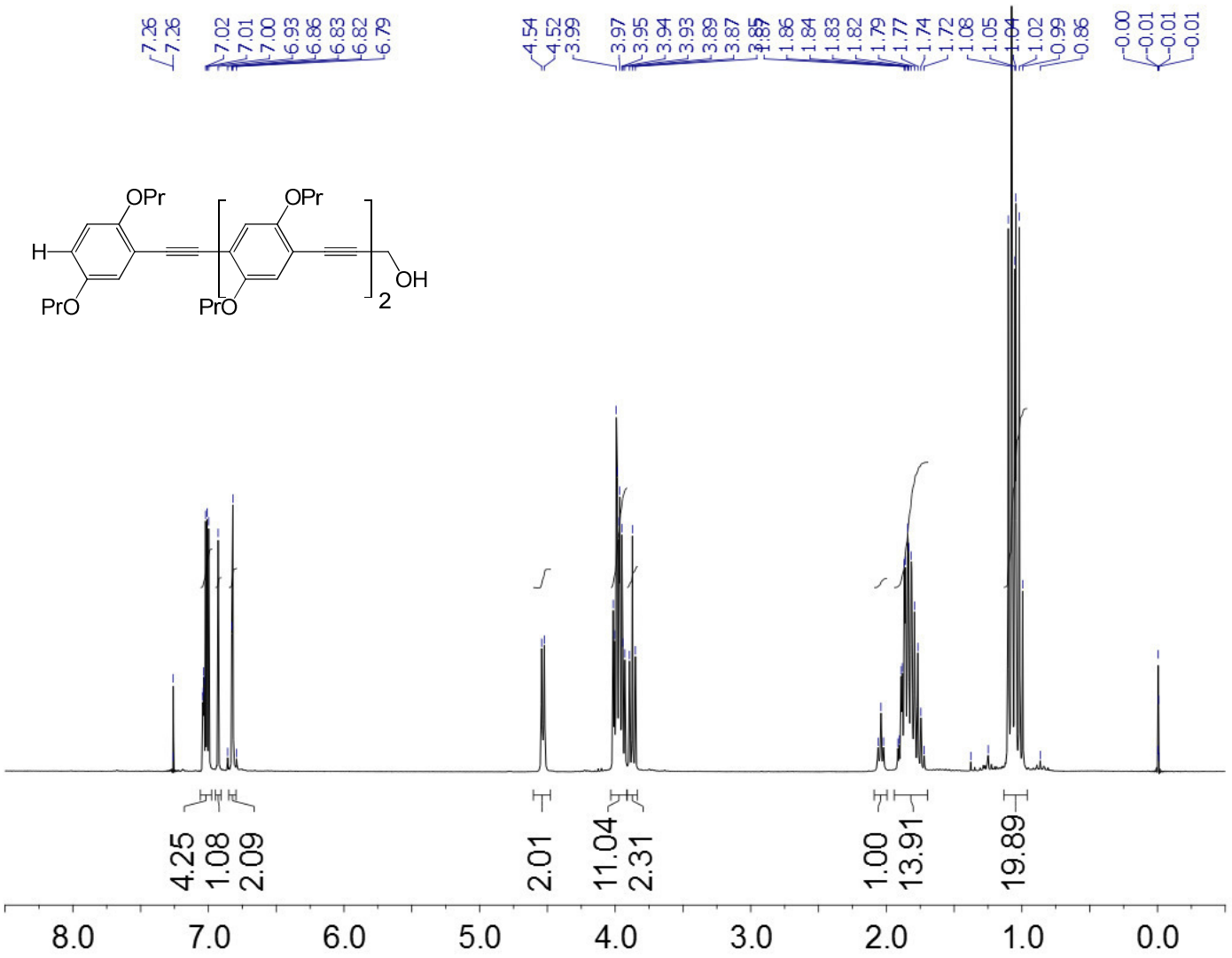

Figure B17. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1-(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-di-proyloxyphenyl)propyn-3-ol, II-6**.

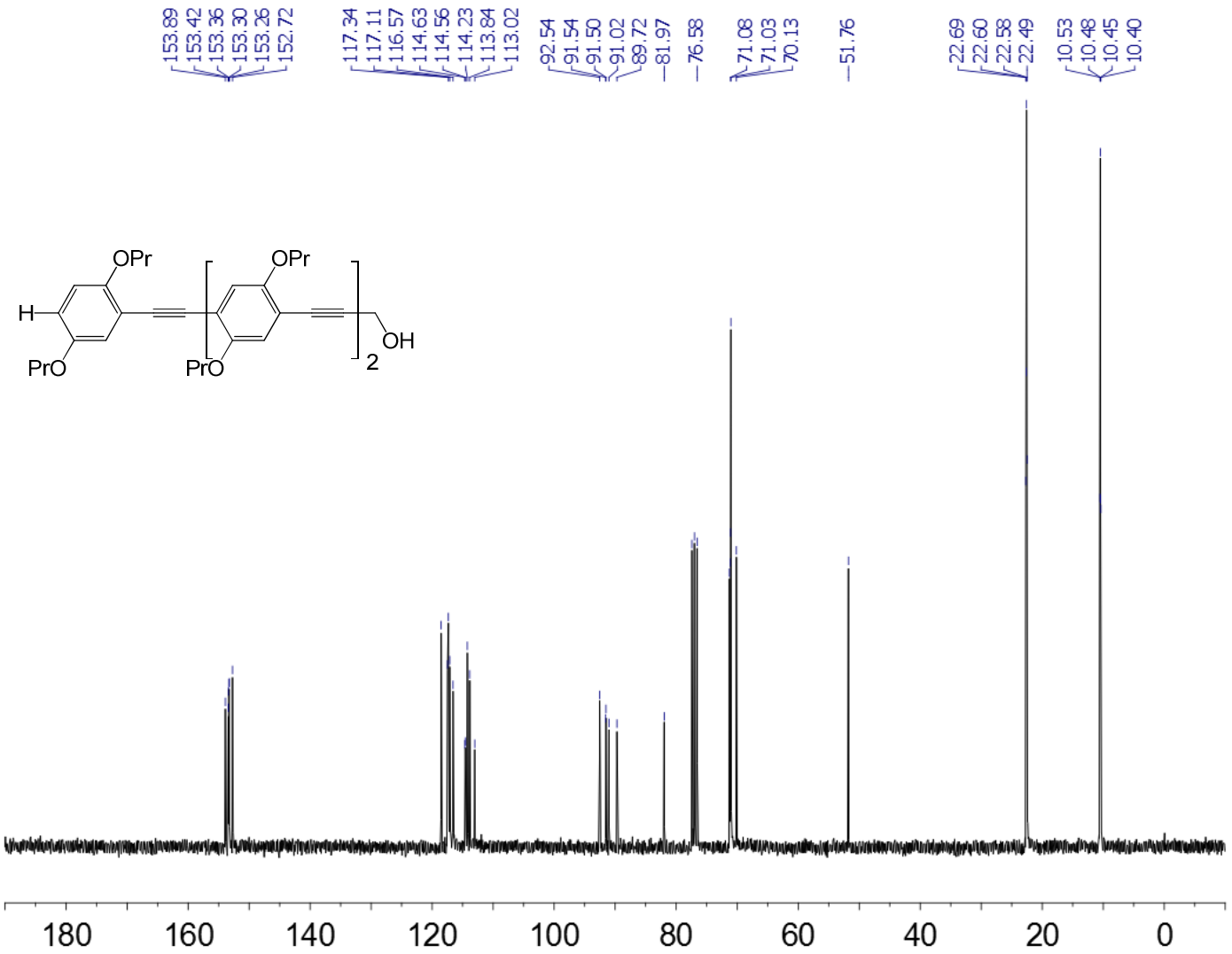

Figure B18. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1-(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-di-proyloxyphenyl)propyn-3-ol, II-6**.

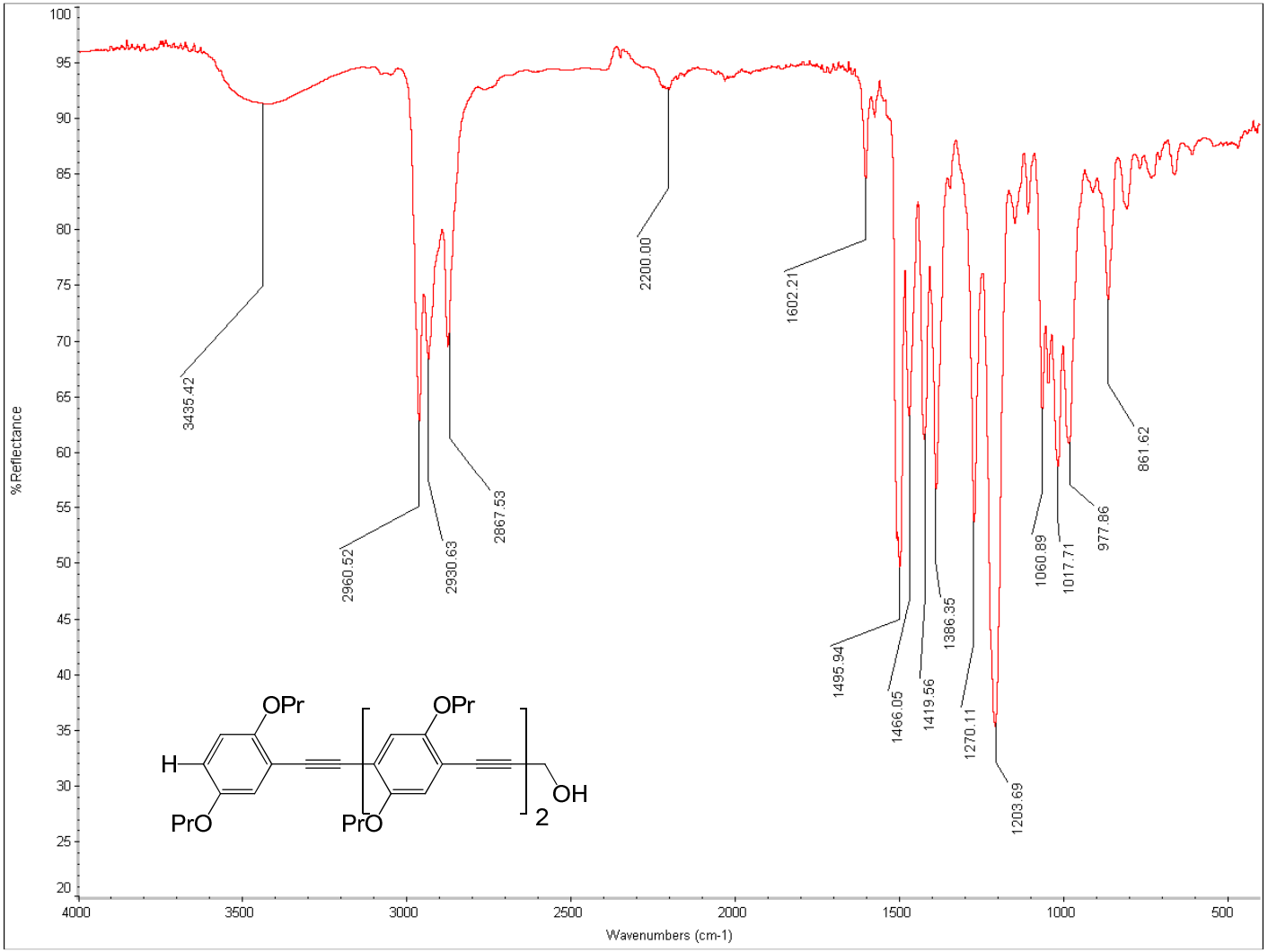

Figure B19. IR (ATIR, neat) of **1-(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-di-proyloxyphenyl)propyn-3-ol, II-6**.

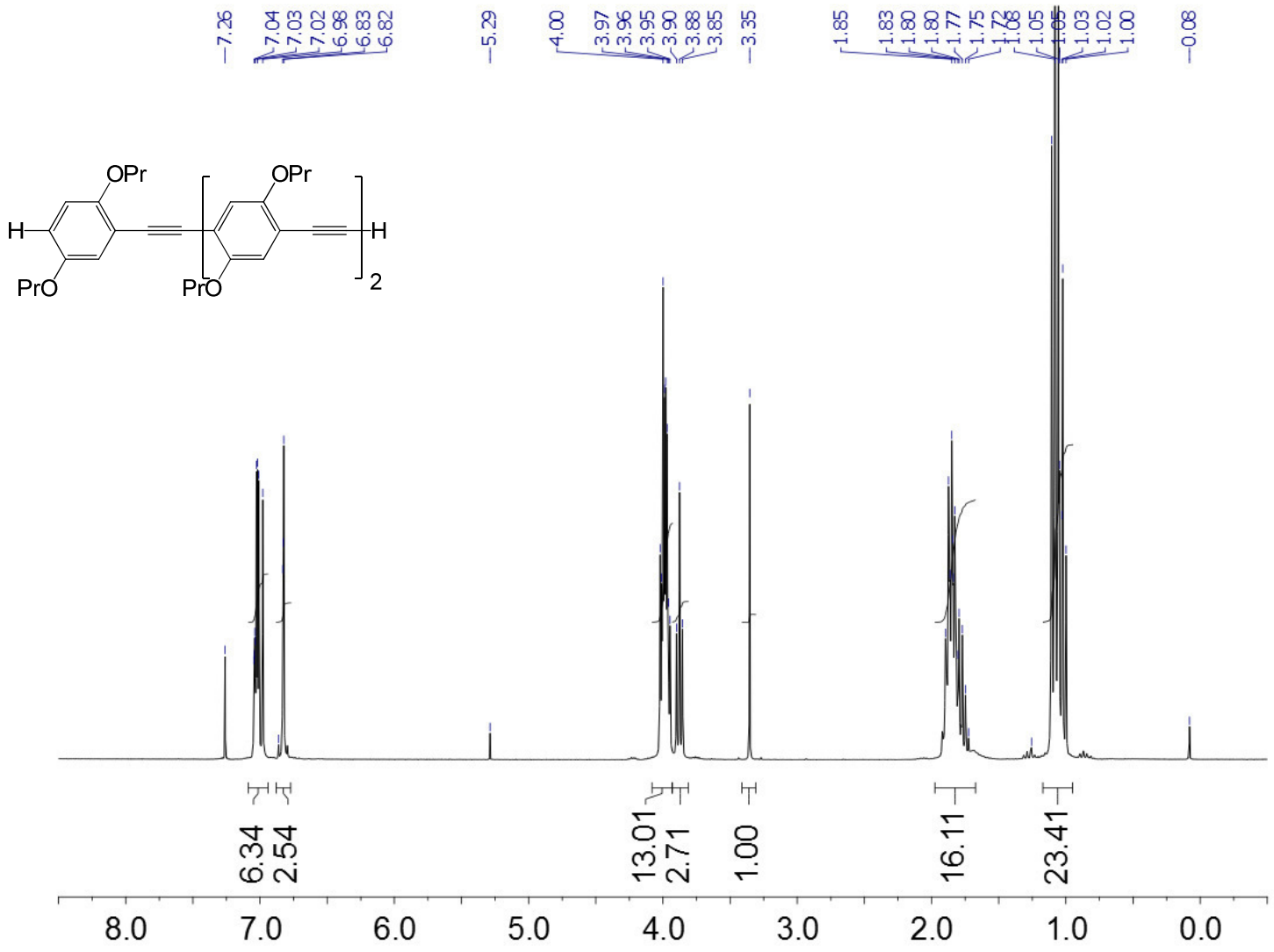

Figure B20. ^{1}HNMR ($CDCl_3$, 300 MHz) of **(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-di-proyloxyphenyl)acetylene, II-7**.

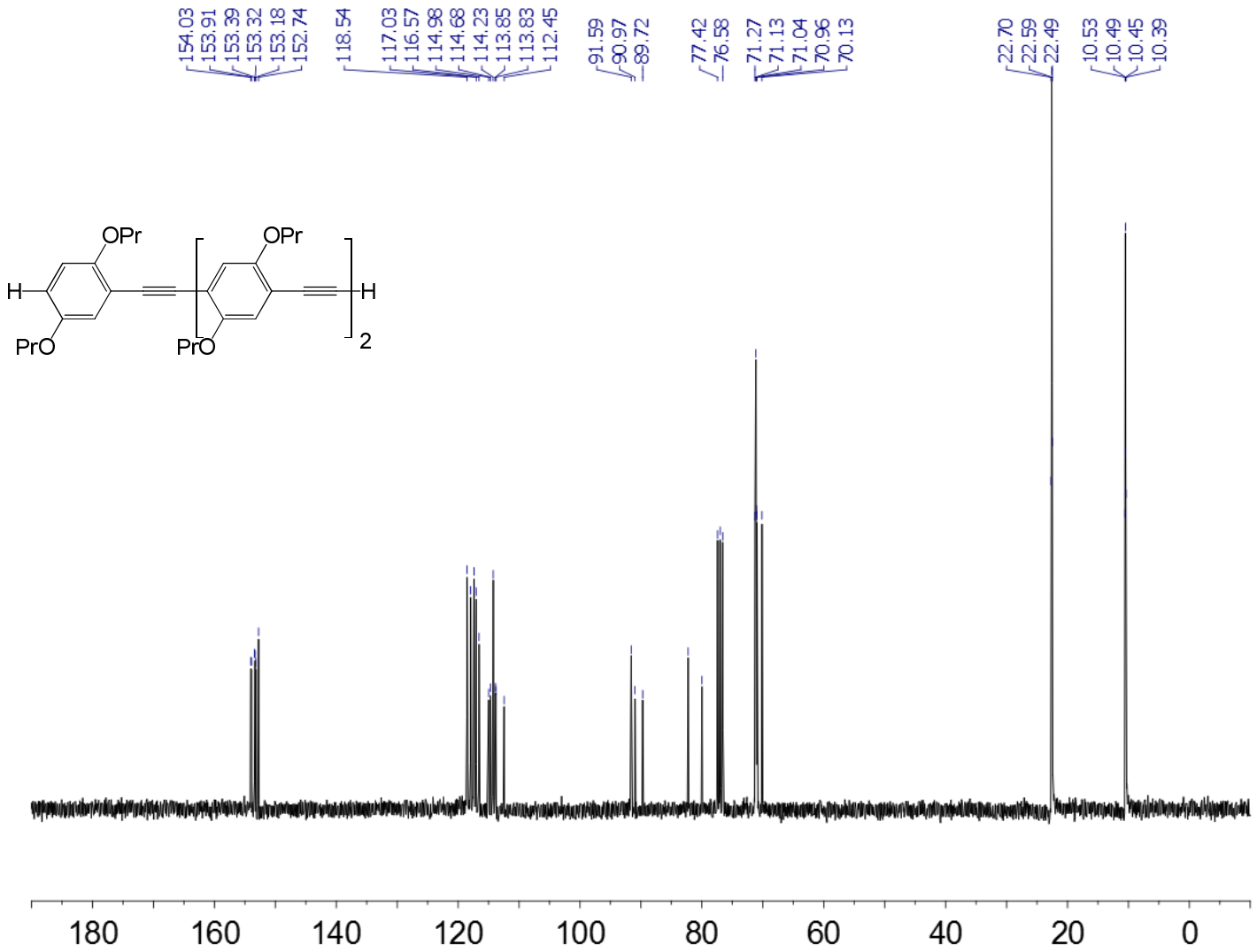

Figure B21. ^{13}CNMR ($CDCl_3$, 300 MHz) of **(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-di-proyloxyphenyl)acetylene, II-7**.

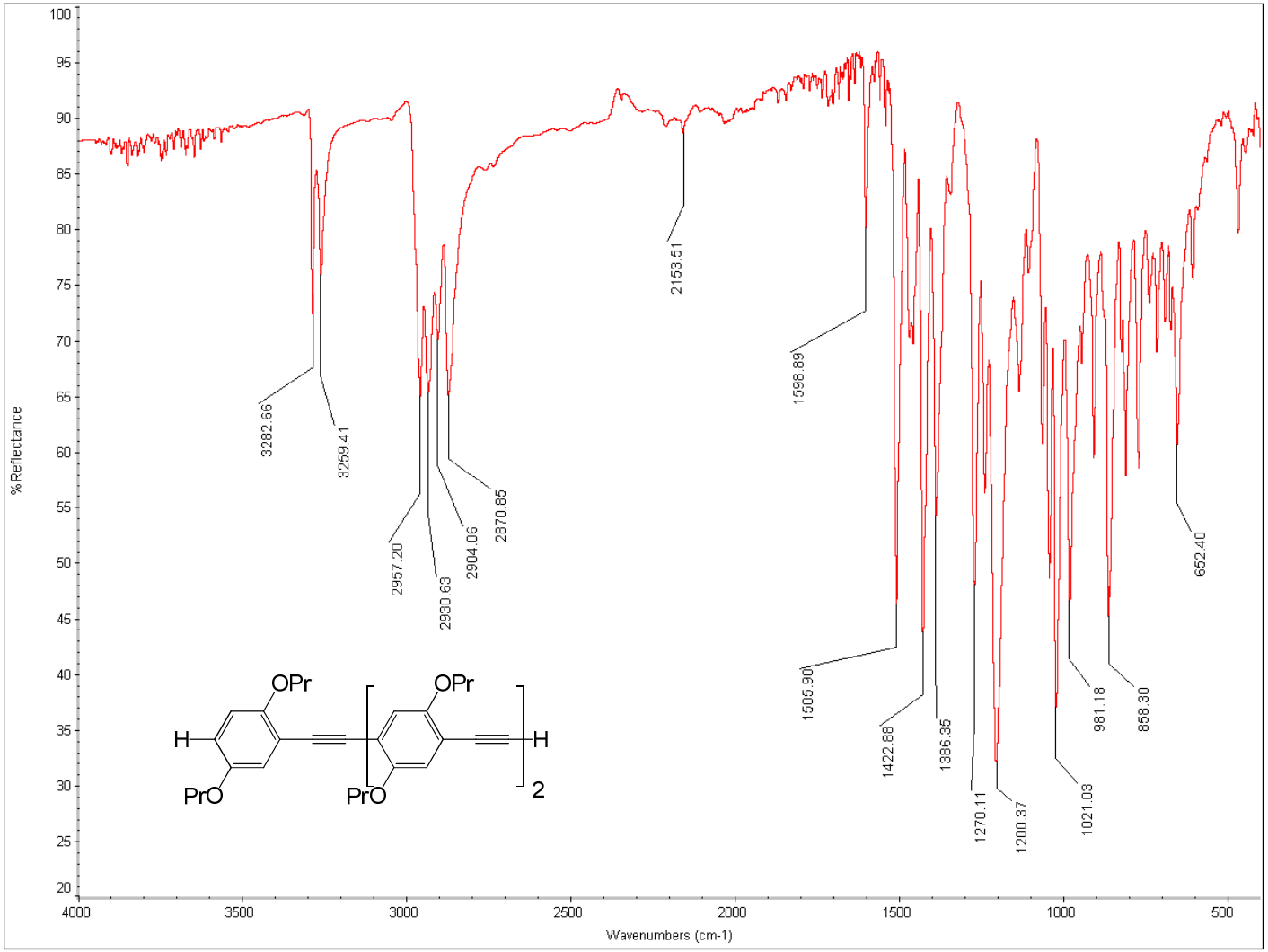

Figure B22. IR (ATIR, neat) of **(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-di-proyloxyphenyl)acetylene, II-7**.

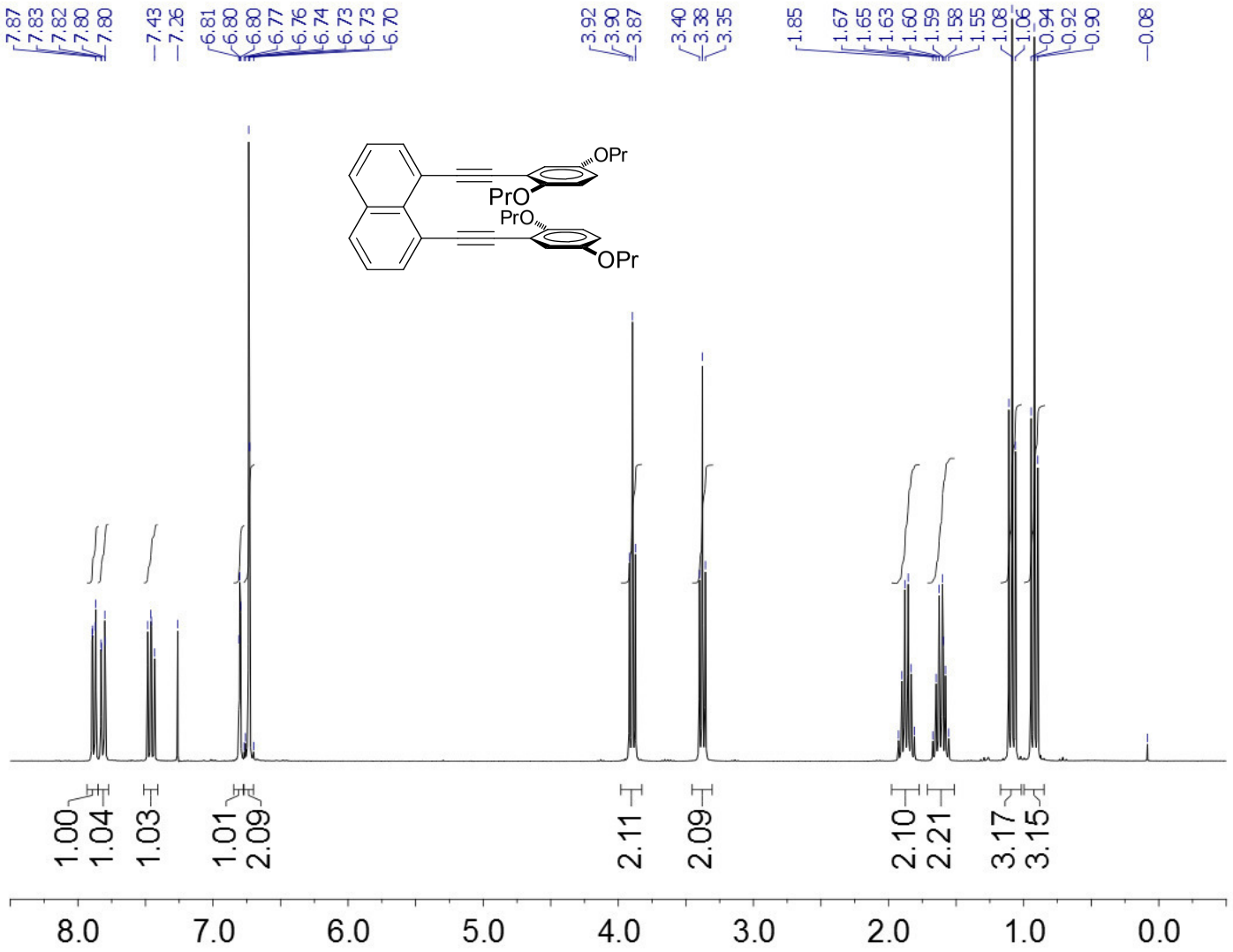

Figure B23. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1,8-(2,5-Dipropyloxyphenylethynyl)naphthalene, II-8**.

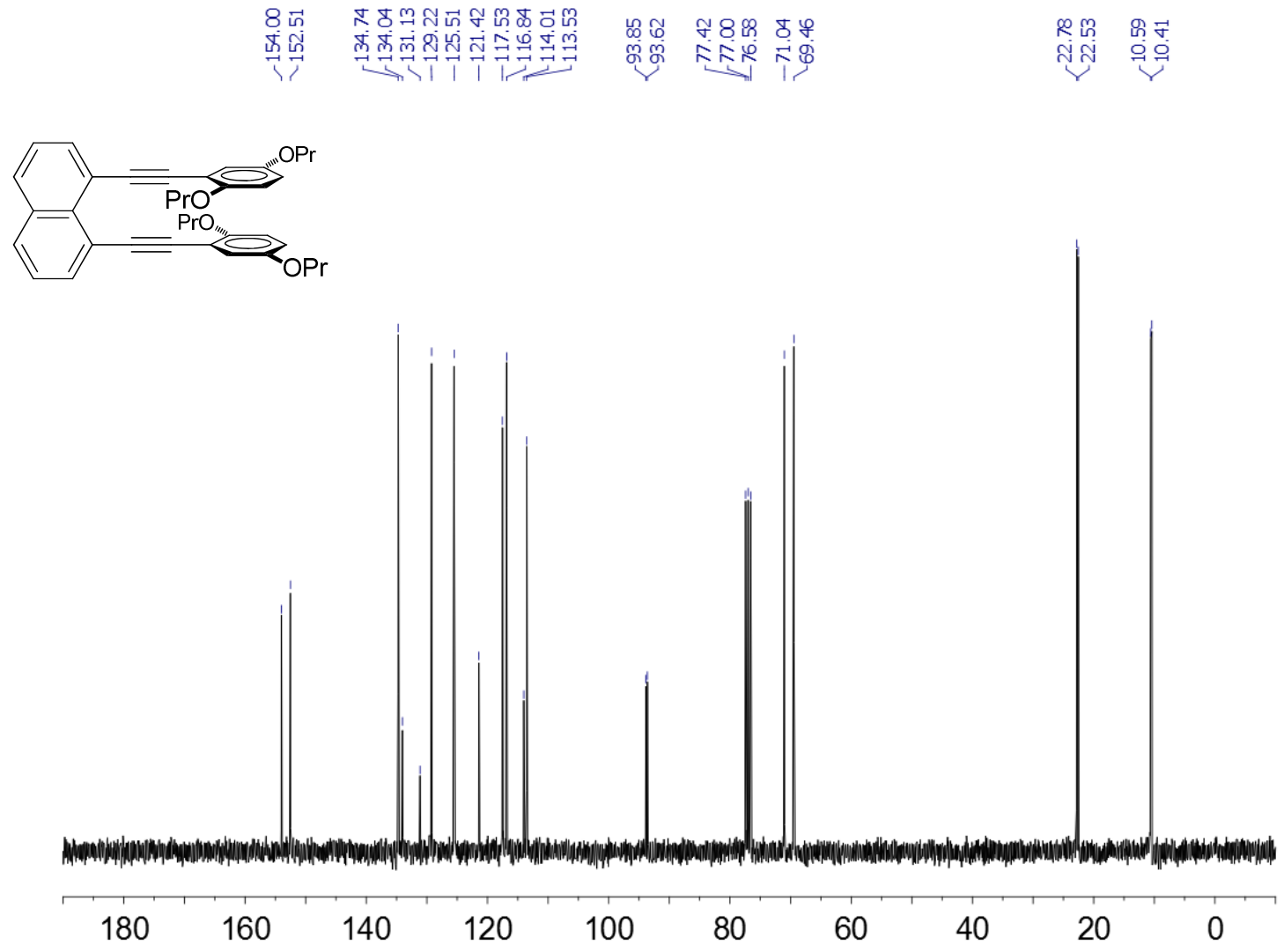

Figure B24. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1,8-(2,5-Dipropyloxyphenylethynyl)naphthalene, II-8**.

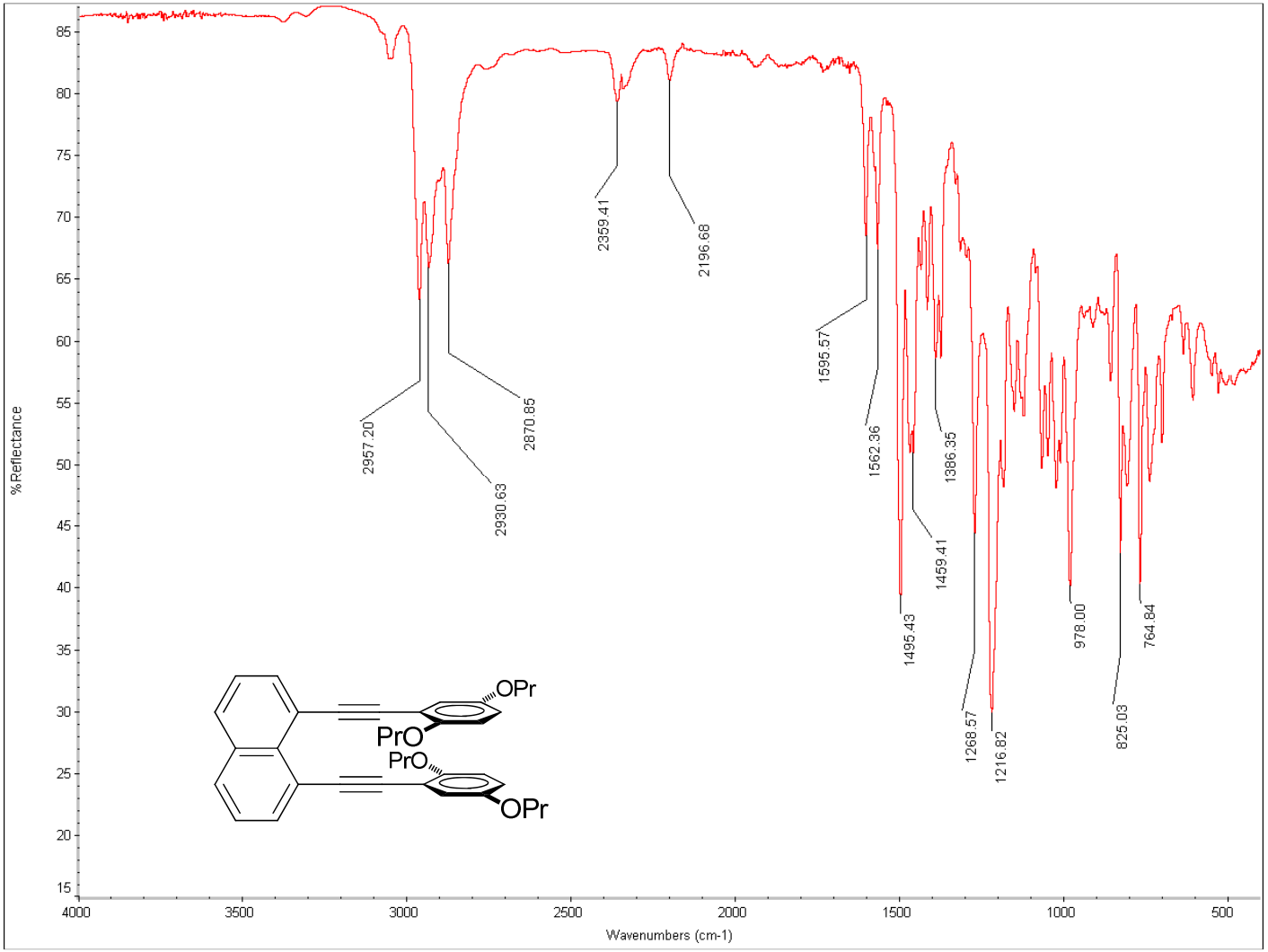

Figure B25. IR (ATIR, neat) of **1,8-(2,5-Dipropyloxyphenylethynyl)naphthalene, II-8**.

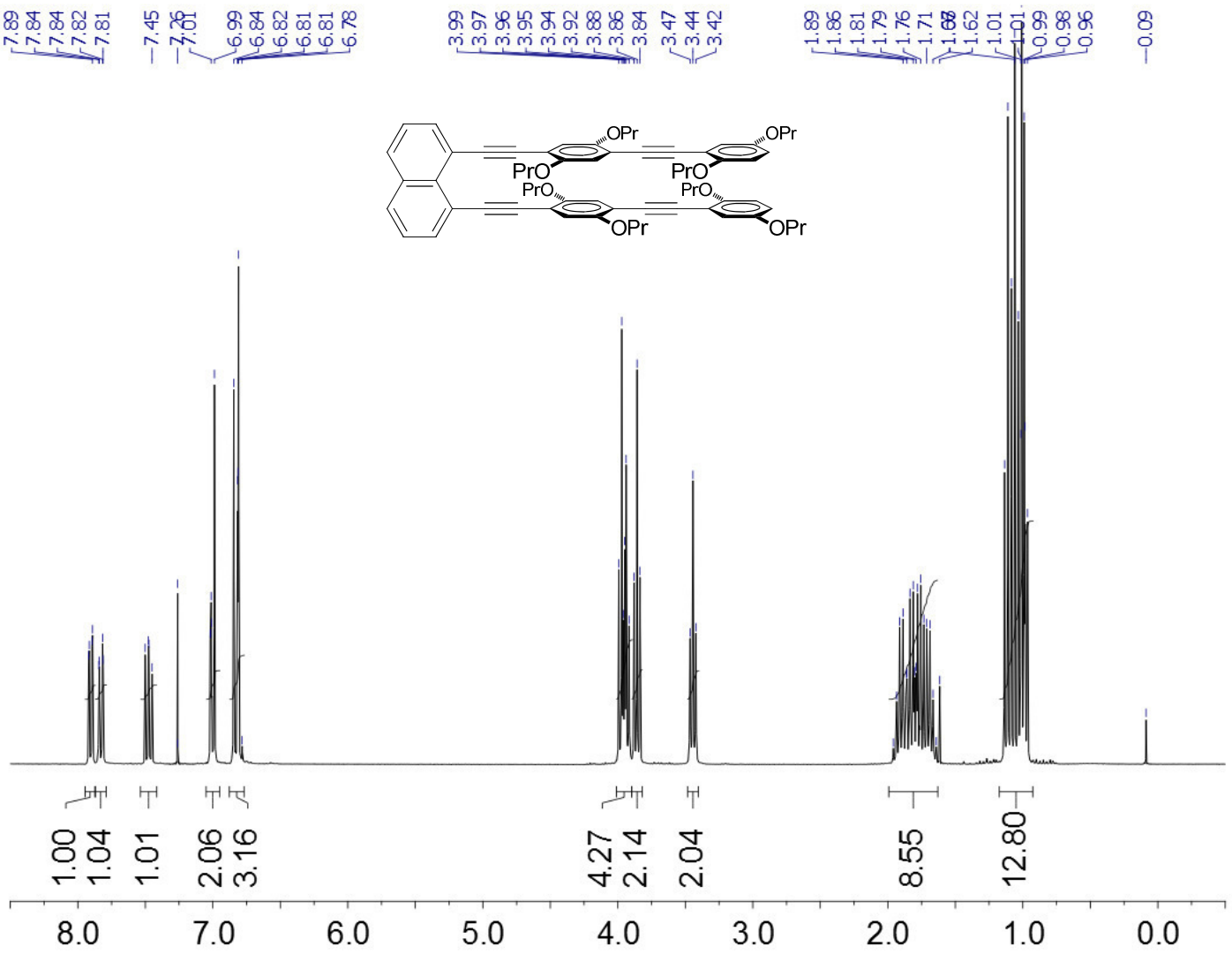

Figure B26. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1,8-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-naphthalene, II-9**.

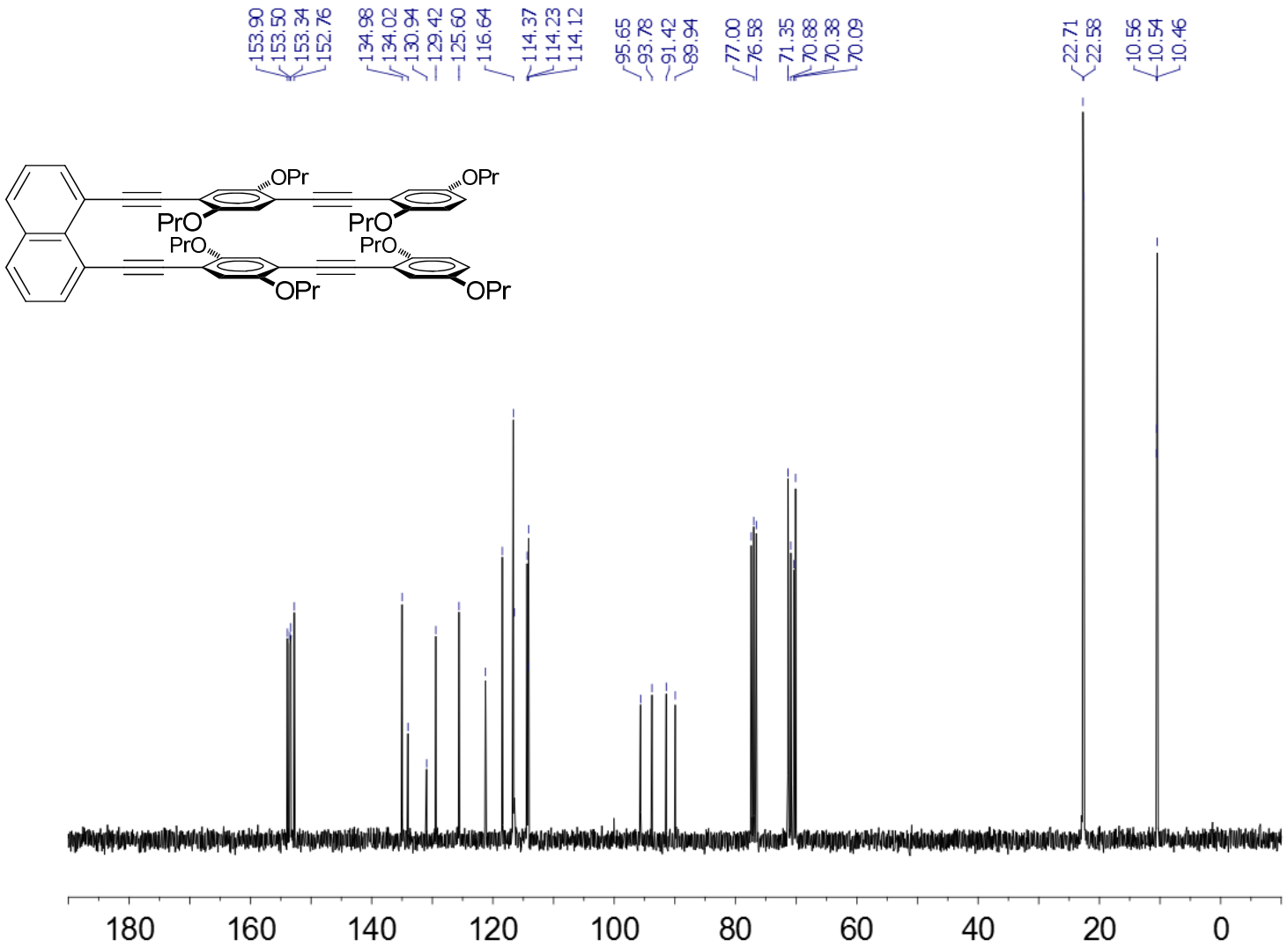

Figure B27. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1,8-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-naphthalene, II-9**.

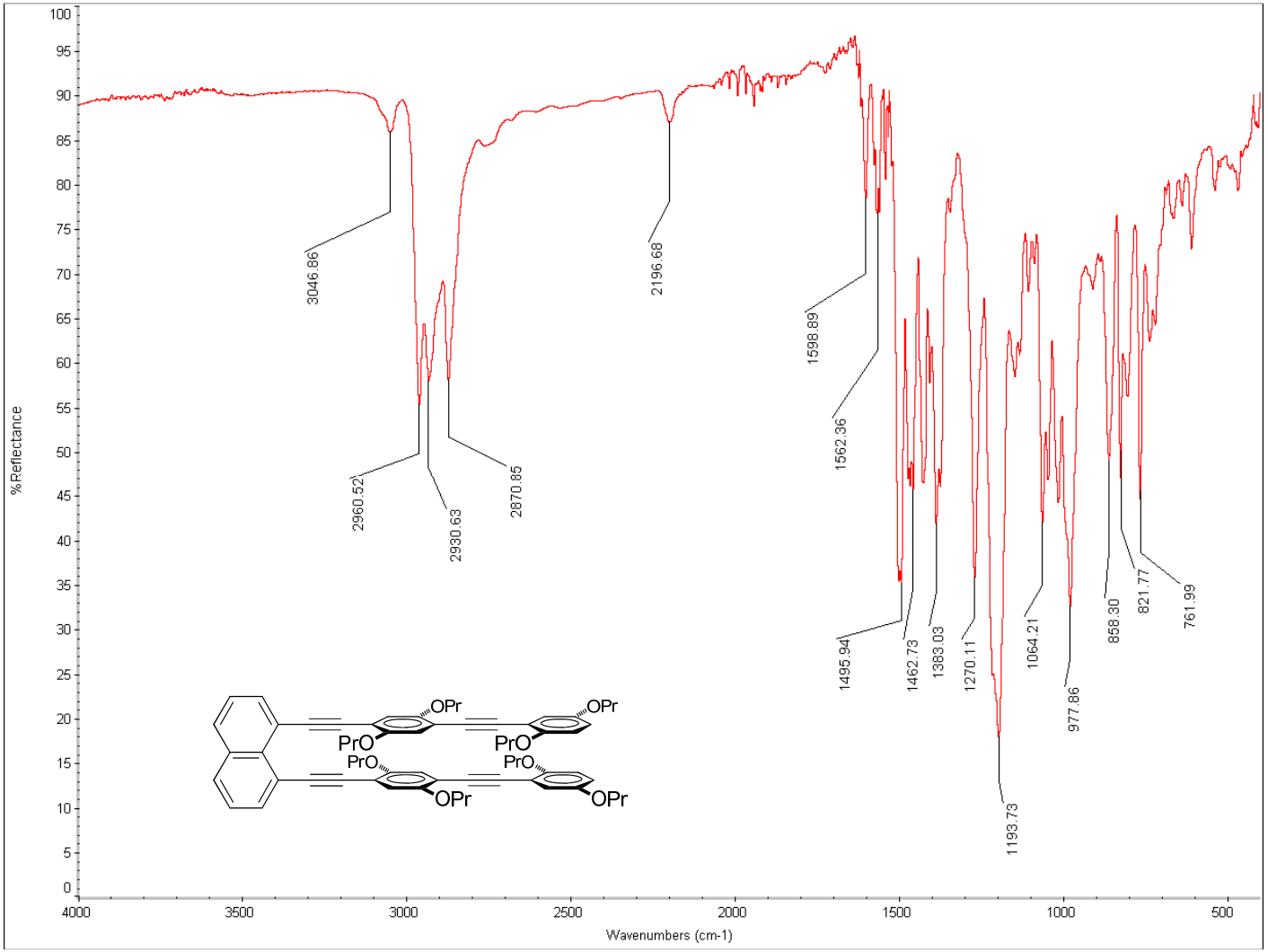

Figure B28. IR (ATIR, neat) of **1,8-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)naphthalene, II-9**.

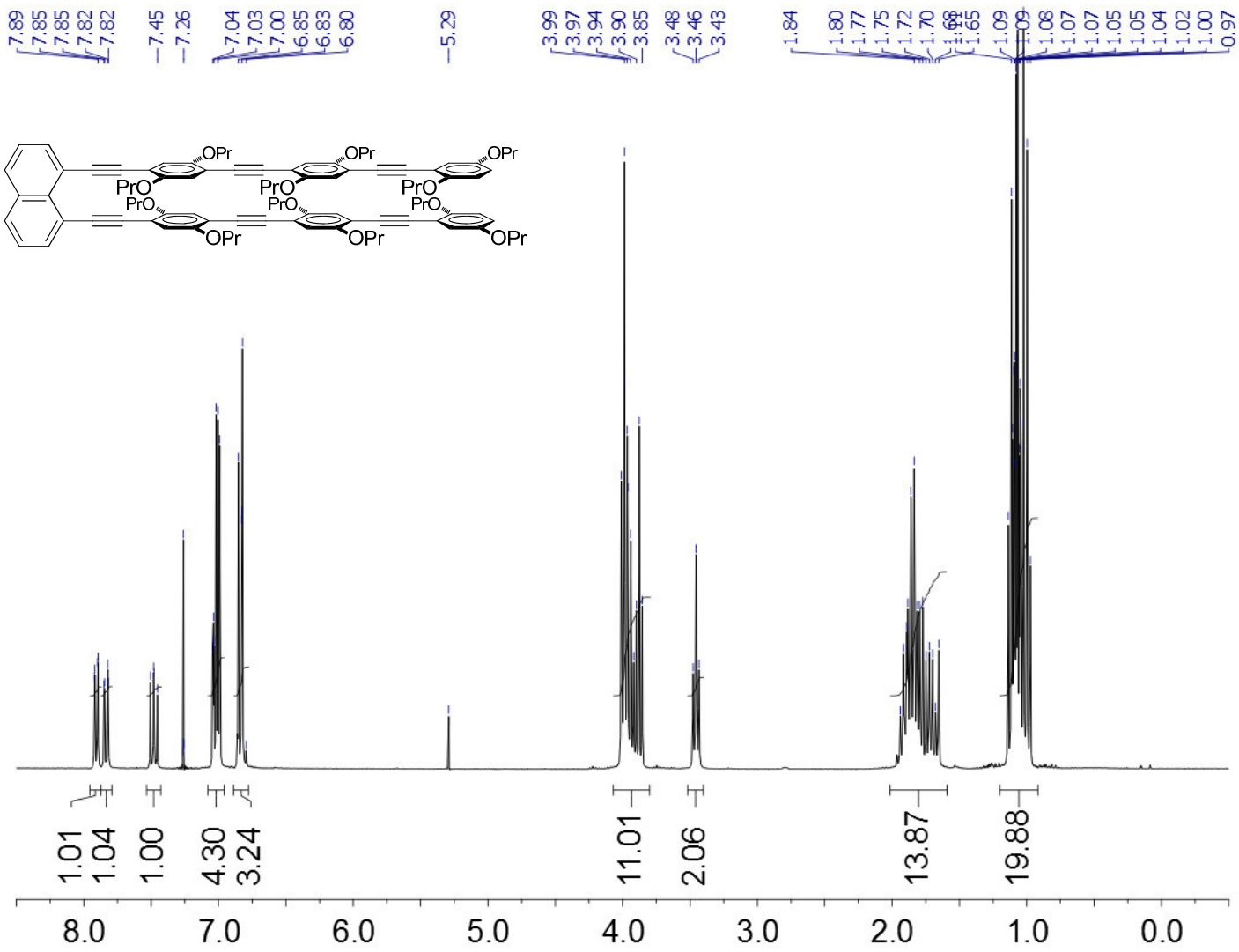

Figure B29. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1,8-(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-diproyloxyphenylethynyl)naphthalene, II-10**.

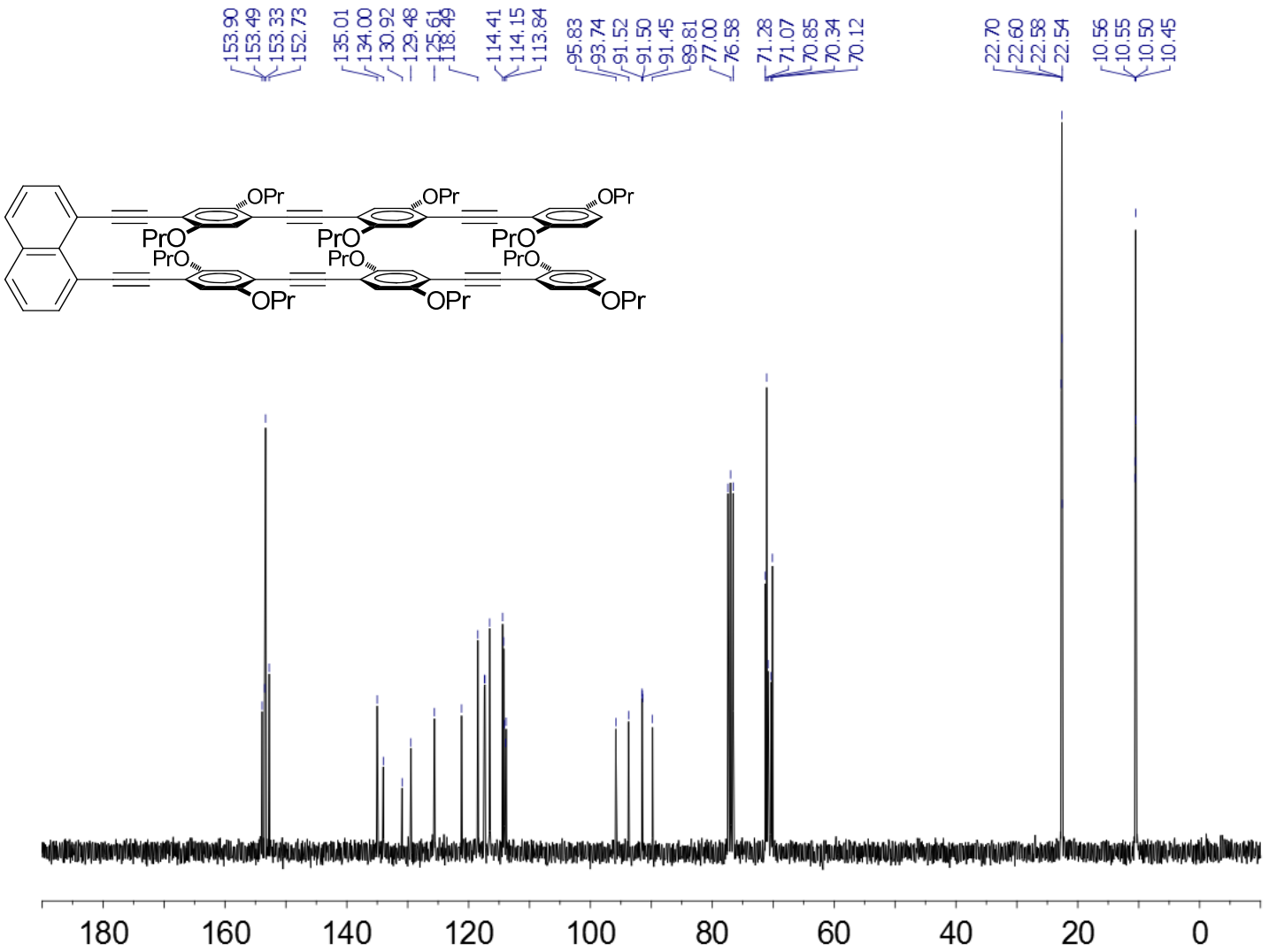

Figure B30. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1,8-(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-diproyloxyphenylethynyl)naphthalene, II-10**.

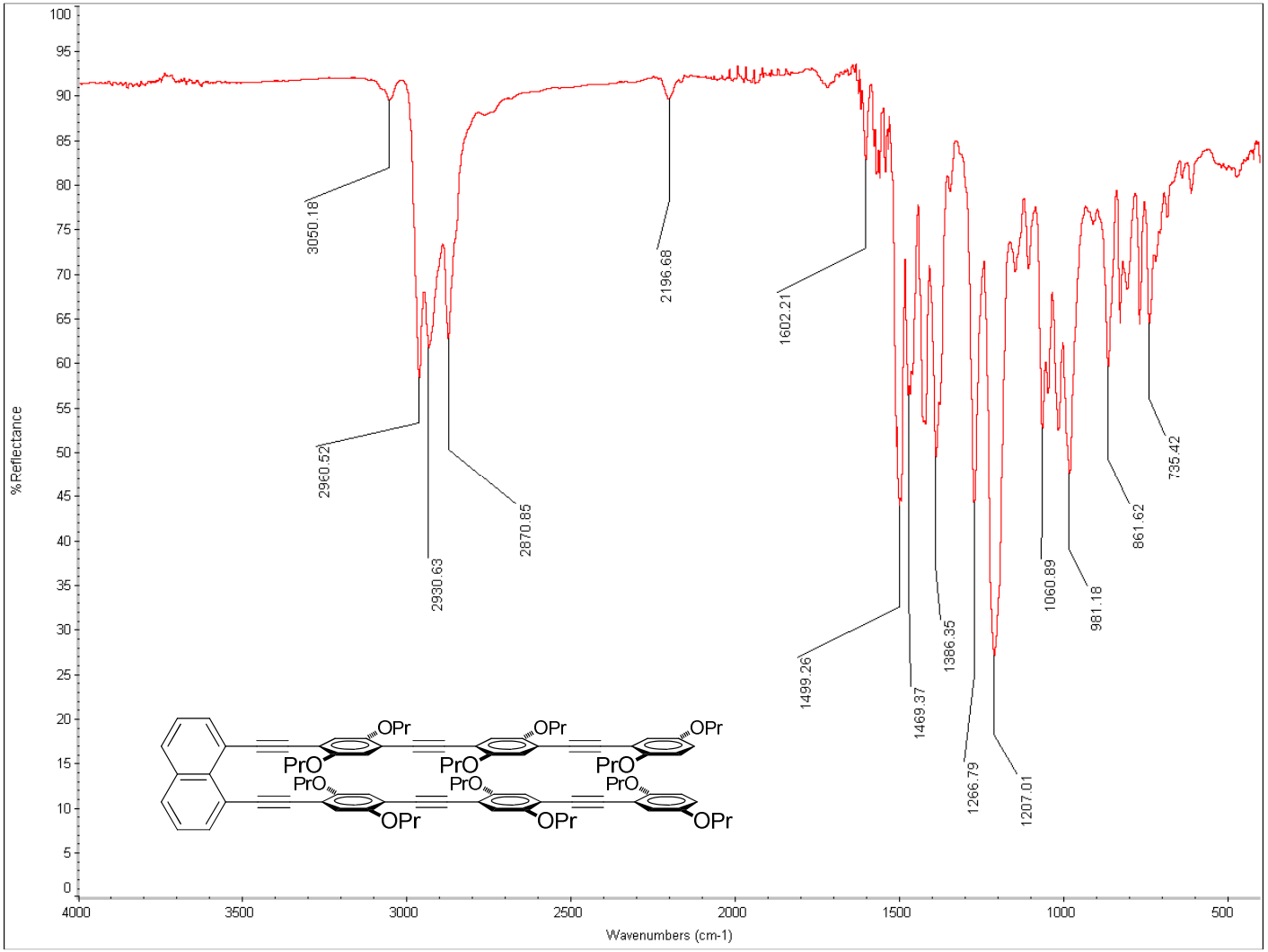

Figure B31. IR (ATIR, neat) of **1,8-(4-(4-(2,5-Dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-2,5-diproyloxyphenylethynyl)naphthalene, II-10**.

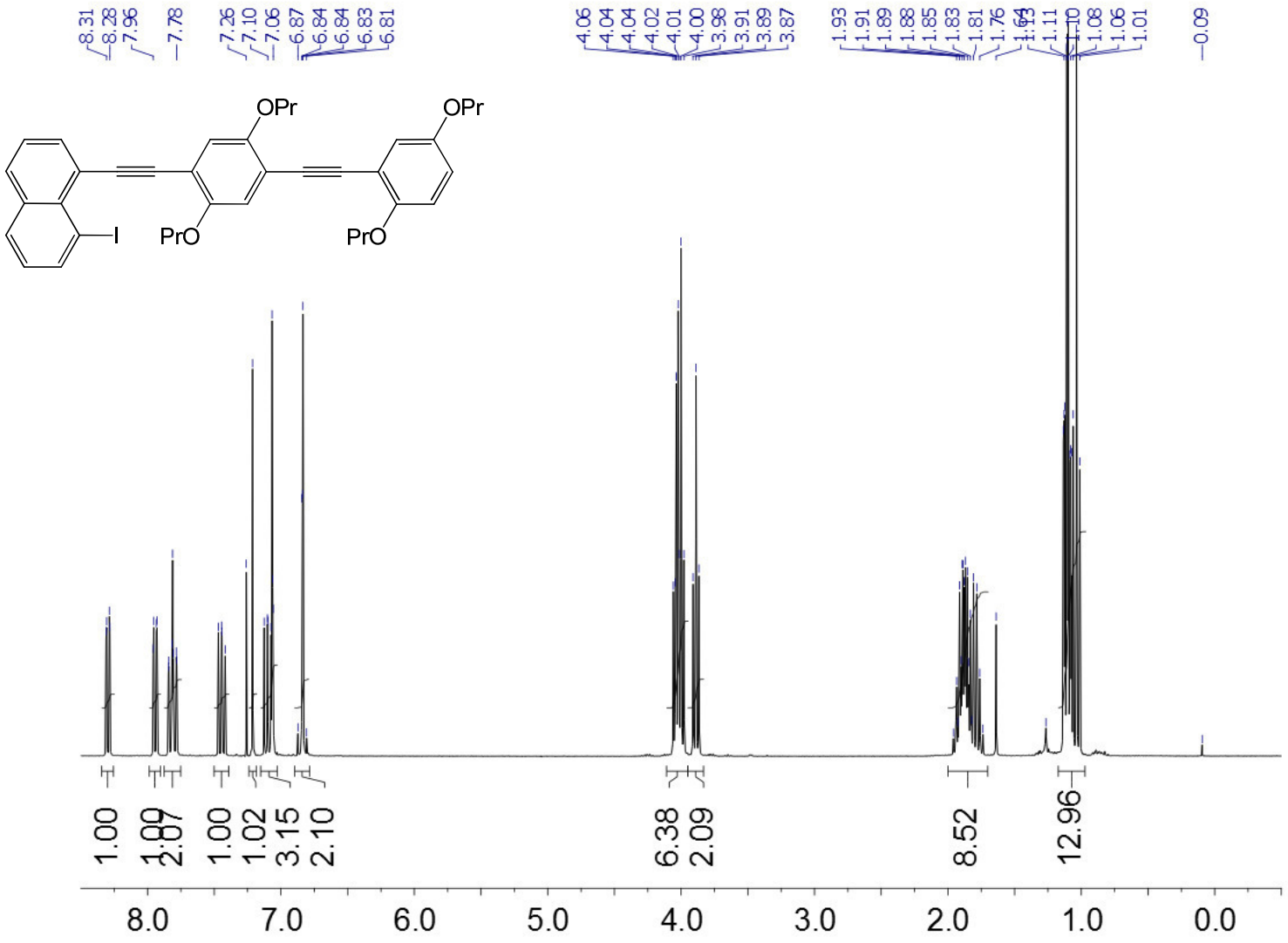

Figure B32. ^{1}HNMR ($CDCl_3$, 300 MHz) of **8-Iodo-1-(4-(2,5-dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-naphthalene, III-1**.

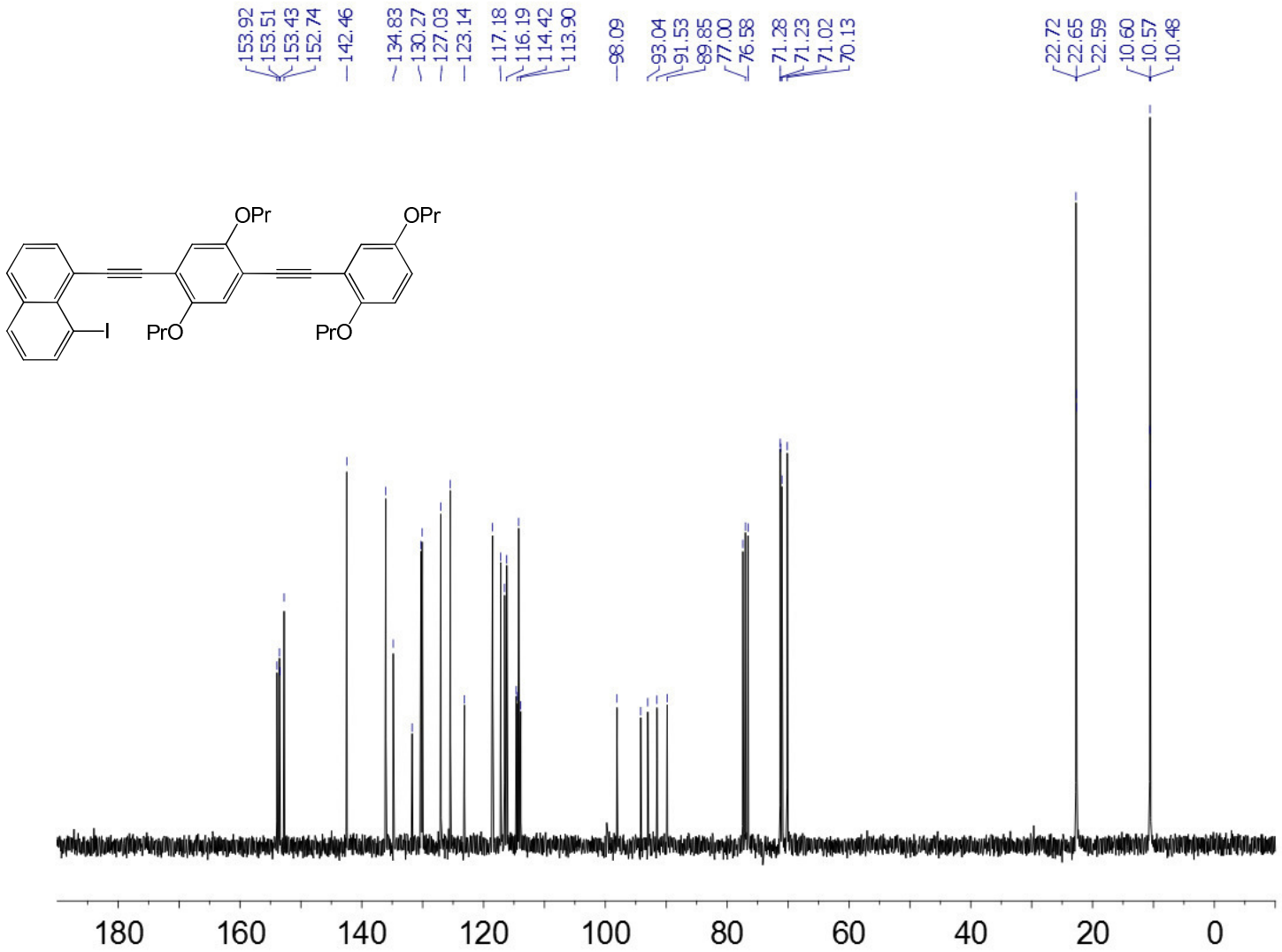

Figure B33. ^{13}CNMR ($CDCl_3$, 300 MHz) of **8-Iodo-1-(4-(2,5-dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-naphthalene, III-1**.

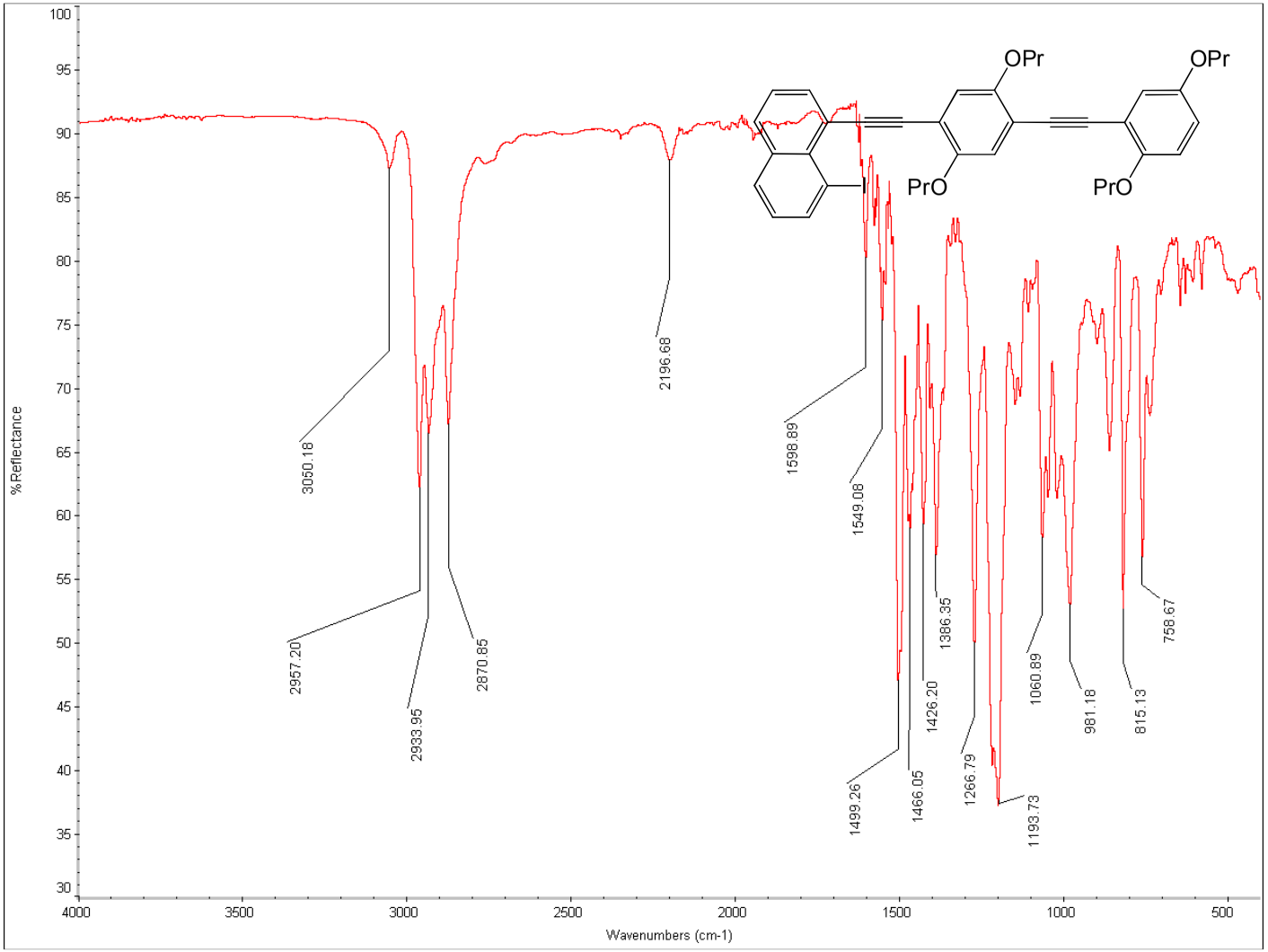

Figure B34. IR (ATIR, neat) of **8-Iodo-1-(4-(2,5-dipropyloxyphenylethynyl)-2,5-dipropyloxyphenylethynyl)-naphthalene, III-1**.

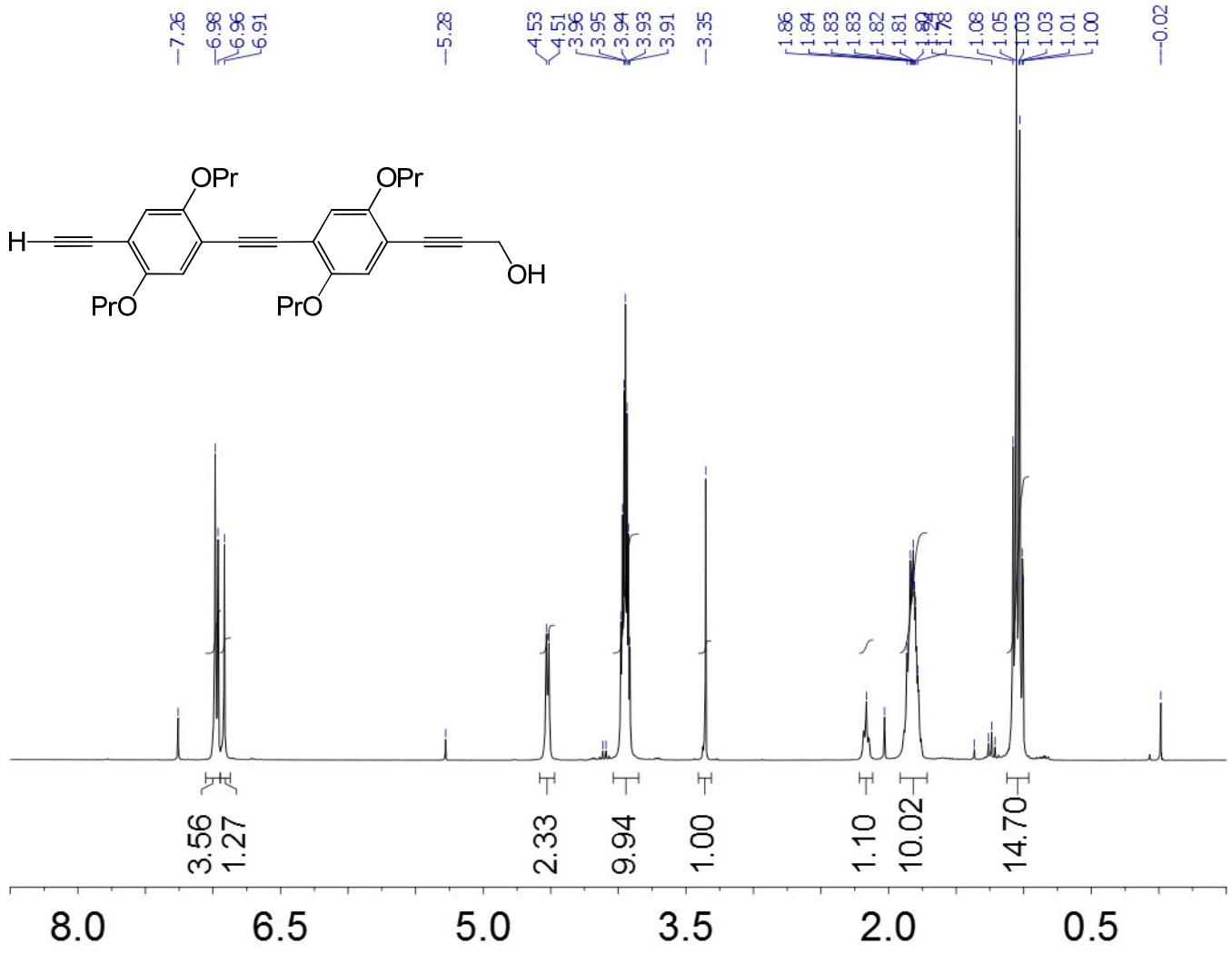

Figure B35. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1-(4-(4-Ethynyl-2,5-dipropyloxyphenylethynyl)-2,5-dipropyloxyphenyl)propyn-3-ol, III-2**.

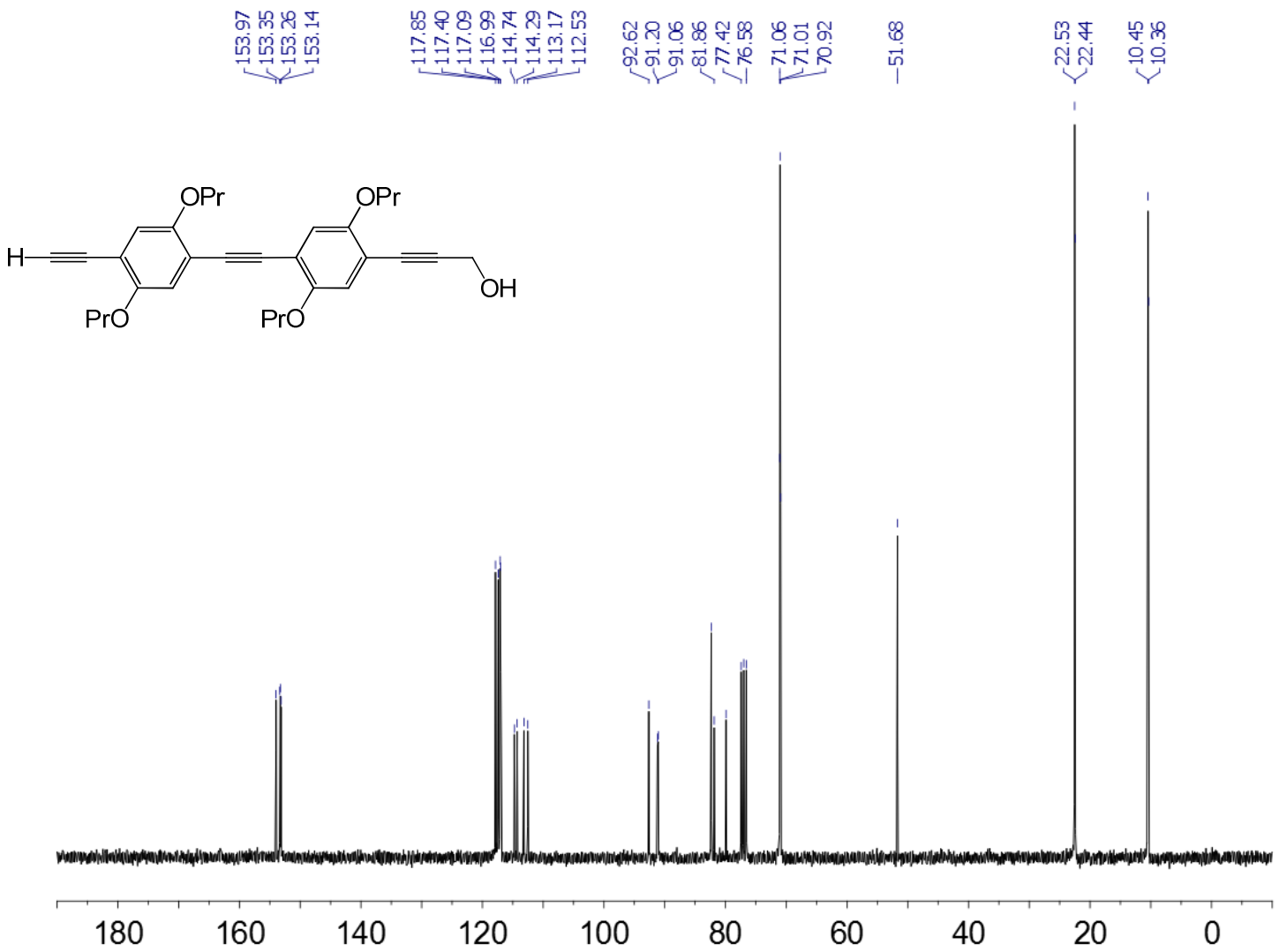

Figure B36. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1-(4-(4-Ethynyl-2,5-dipropyloxyphenylethynyl)-2,5-dipropyloxyphenyl)propyn-3-ol, III-2**.

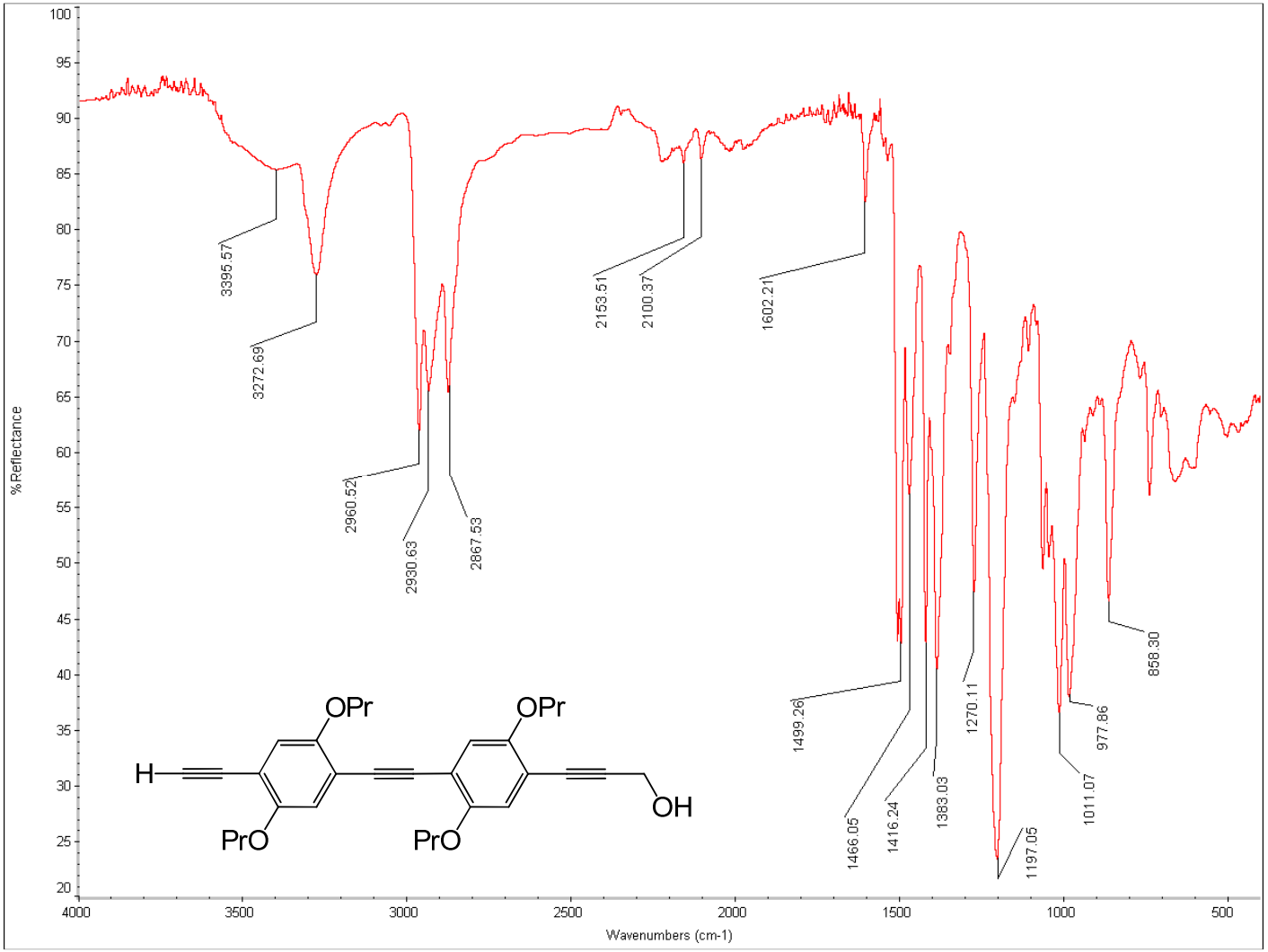

Figure B37. IR (ATIR, neat) of **1-(4-(4-Ethynyl-2,5-dipropyloxyphenylethynyl)-2,5-dipropyloxyphenyl)propyn-3-ol, III-2**.

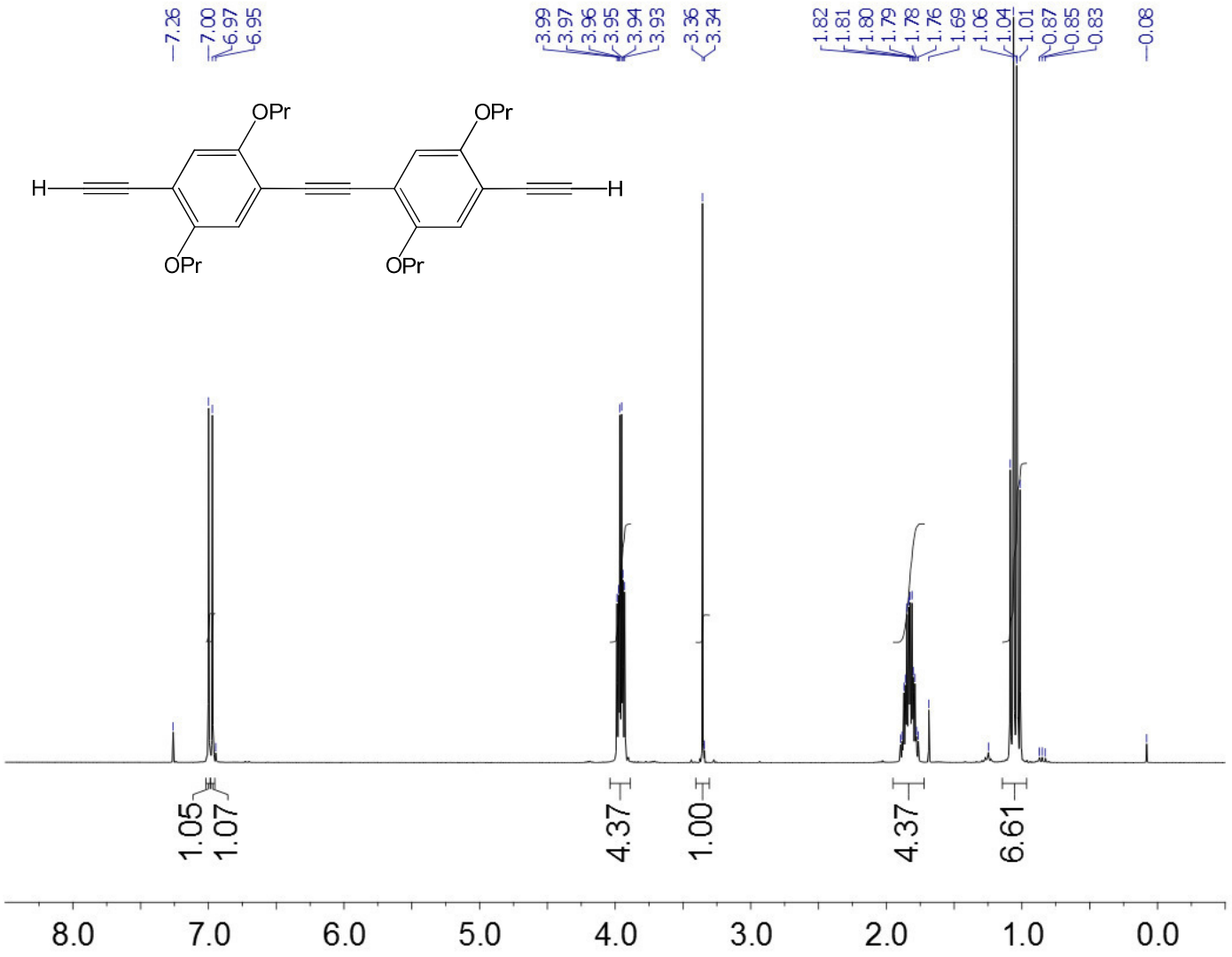

Figure B38. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1,2-(2,5-Dipropyloxyphenylacetylene)ethylene, III-3**.

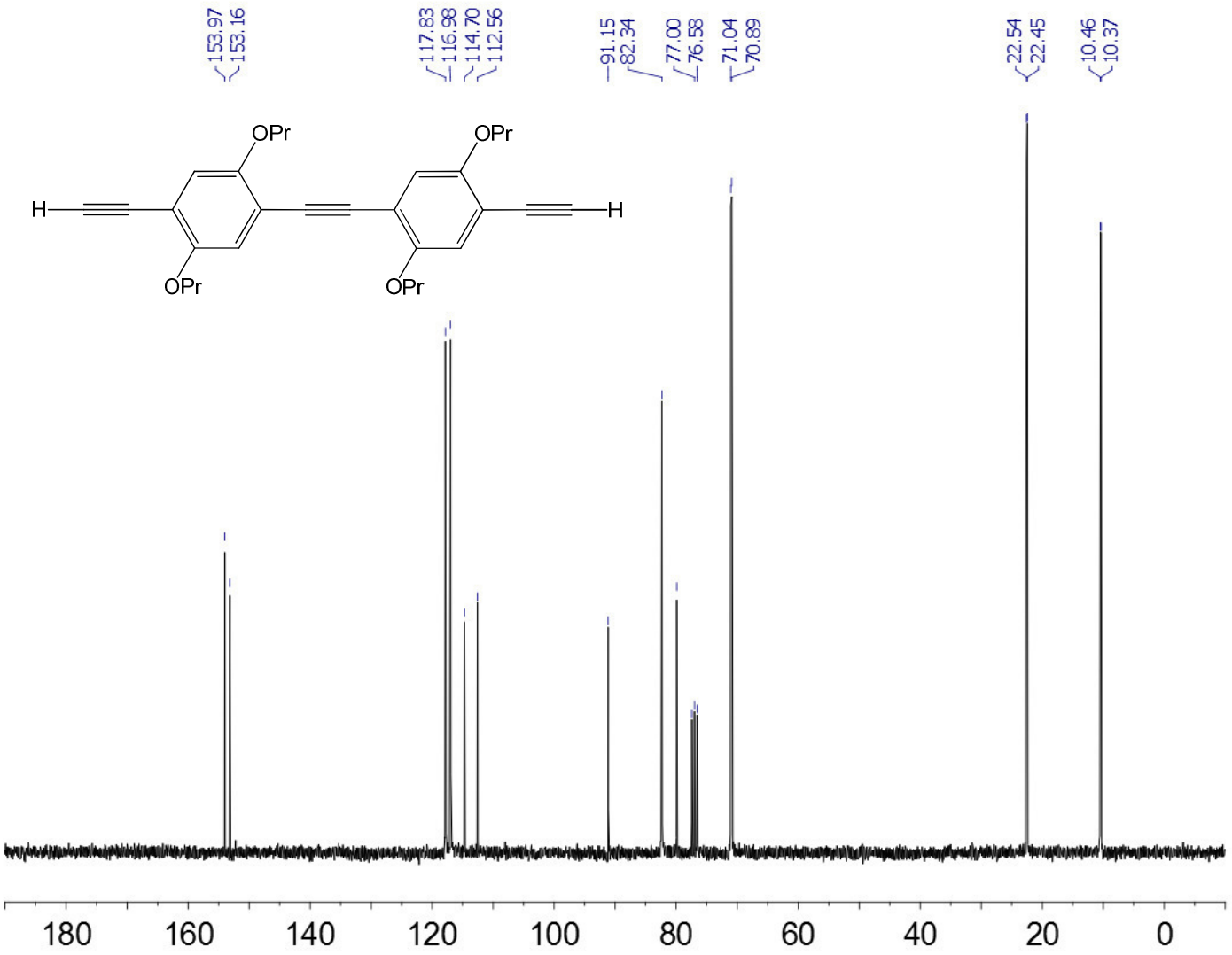

Figure B39. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1,2-(2,5-Dipropyloxyphenylacetylene)ethylene, III-3**.

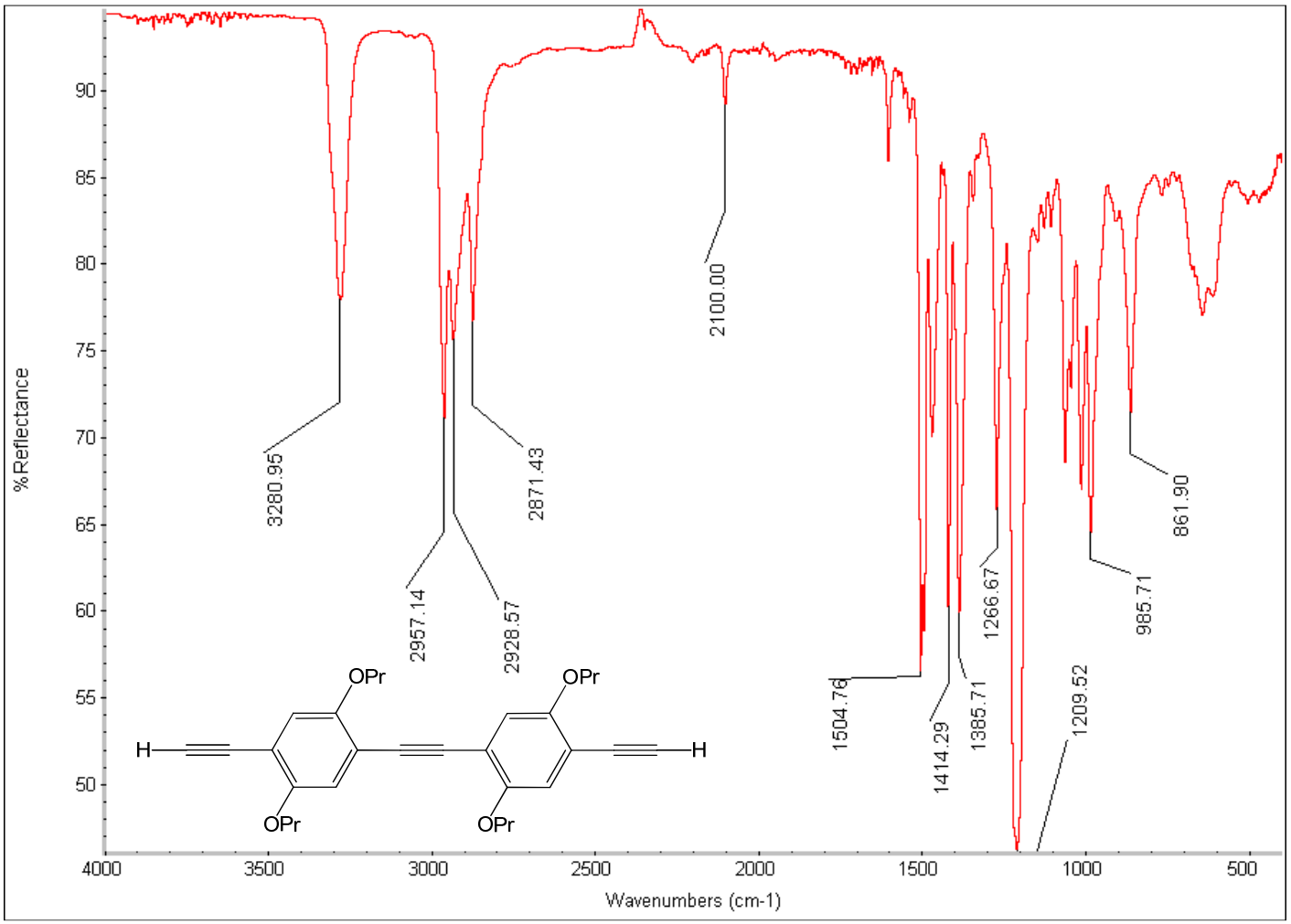

Figure B40. IR (ATIR, neat) of **1,2-(2,5-Dipropyloxyphenylacetylene)ethylene, III-3**.

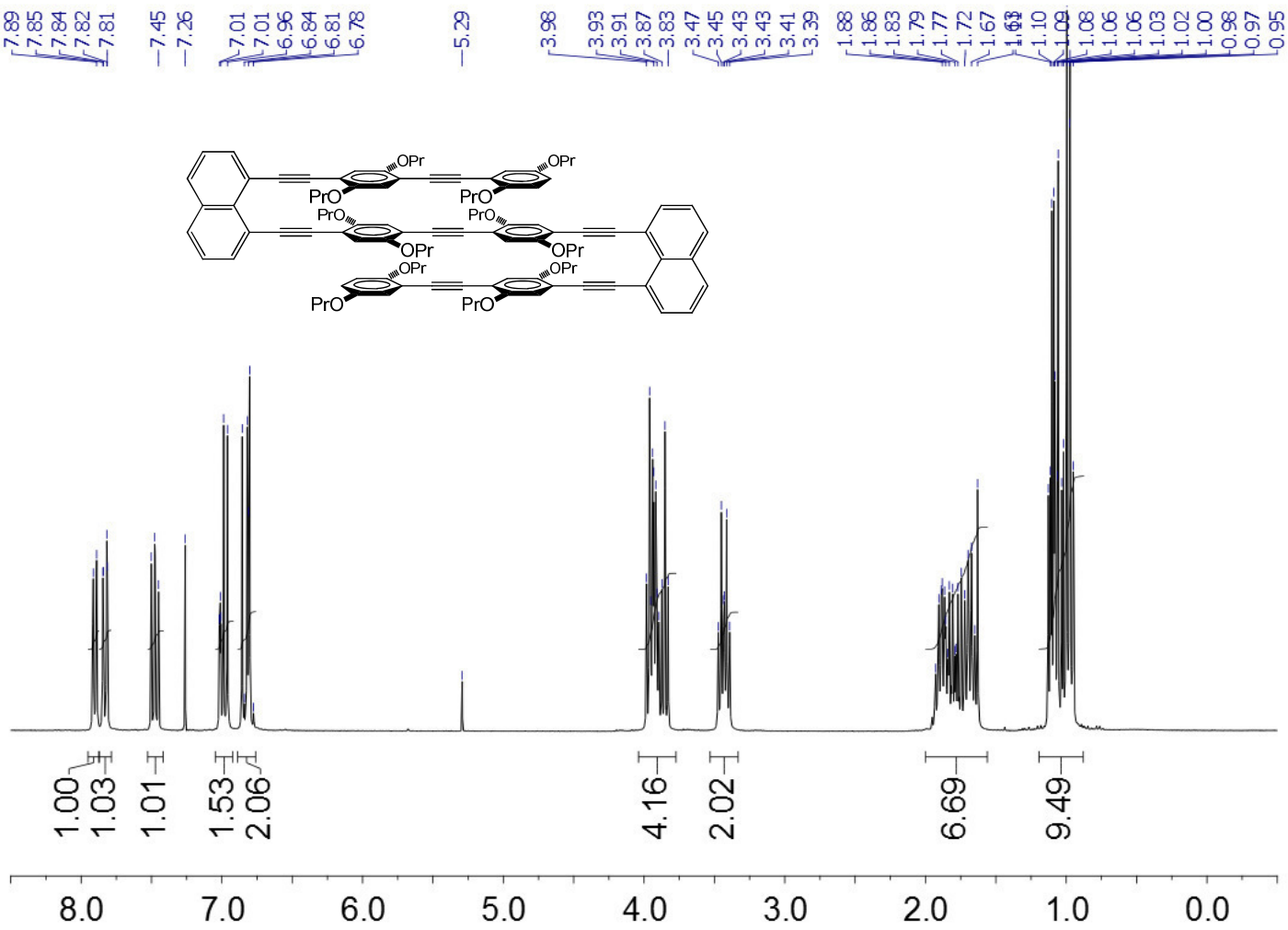

Figure B41. ^{1}HNMR ($CDCl_3$, 300 MHz) of **8-Dinaphthyl-(4-(2,5-dipropyloxyphenylethynyl)-2,5-(dipropyloxyphenylethynyl)-1-((2,5-dipropyloxyphenylethynyl)ethylene), III-4**.

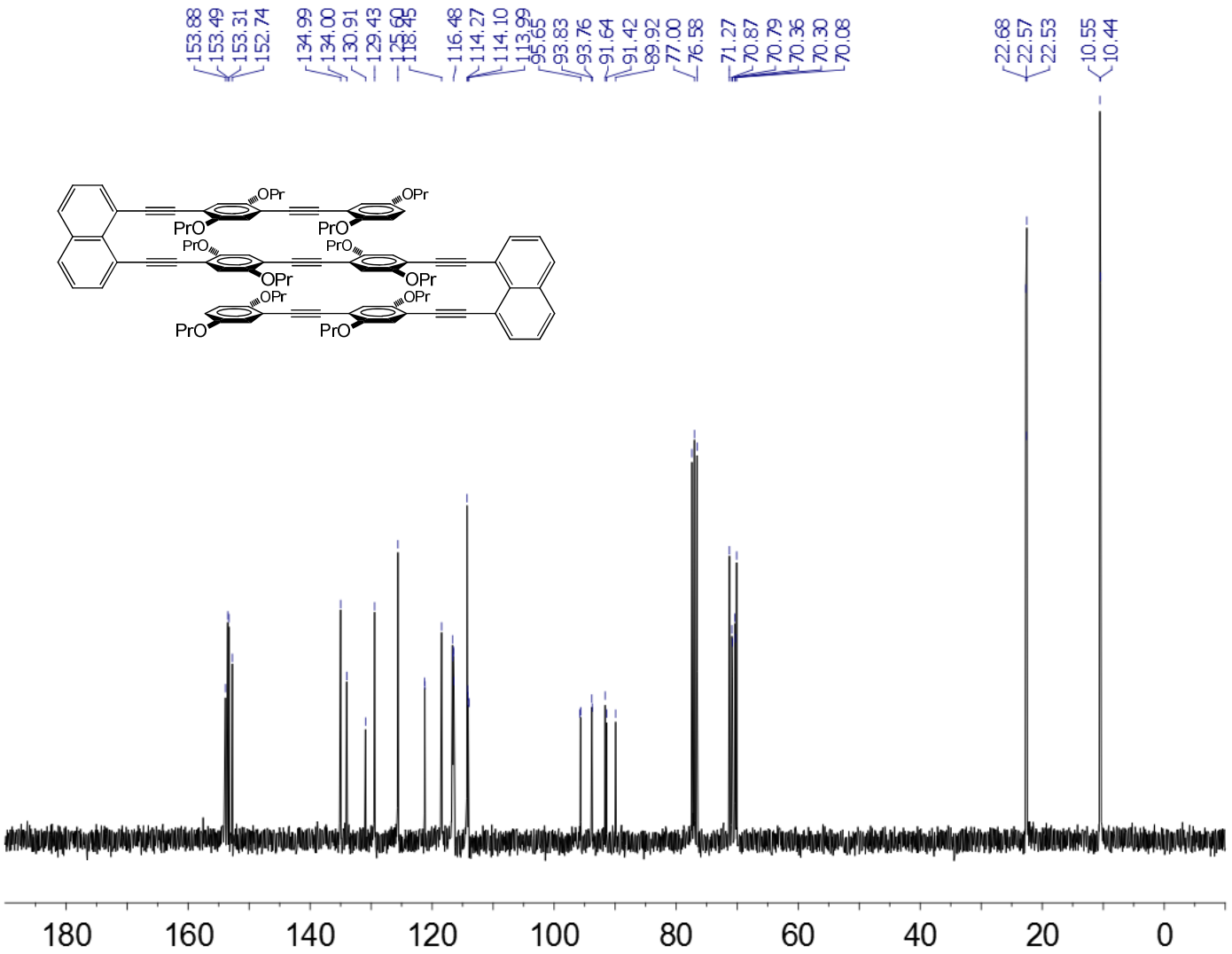

Figure B42. ^{13}CNMR ($CDCl_3$, 300 MHz) of **8-Dinaphthyl-(4-(2,5-dipropyloxyphenylethynyl)-2,5-(dipropyloxyphenylethynyl)-1-((2,5-dipropyloxyphenylethynyl)ethylene), III-4**.

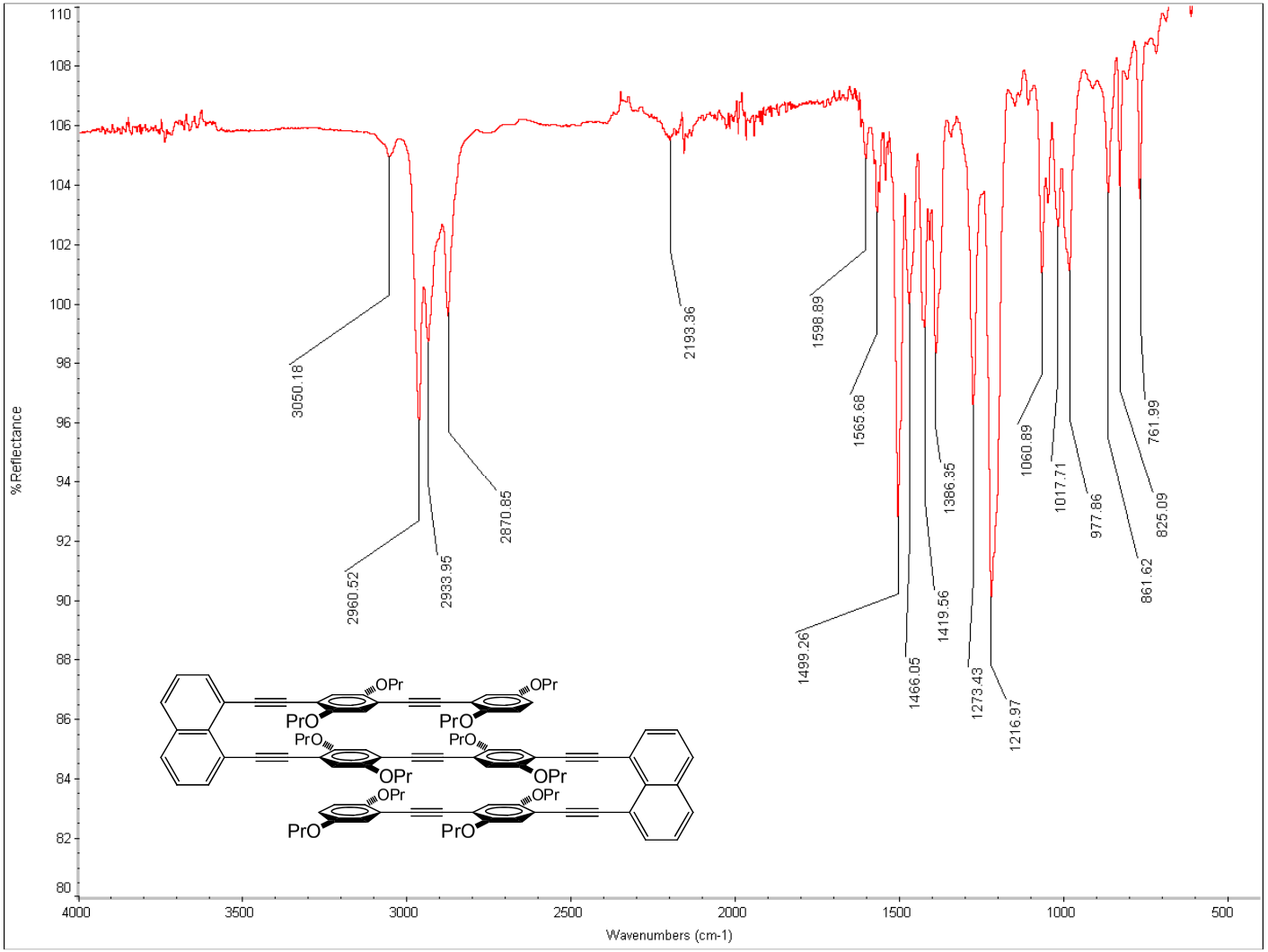

Figure B43. IR (ATIR, neat) of **8-Dinaphthyl-(4-(2,5-dipropyloxyphenylethynyl)-2,5-(dipropyloxyphenylethynyl)-1-((2,5-dipropyloxyphenylethynyl)ethylene), III-4**.

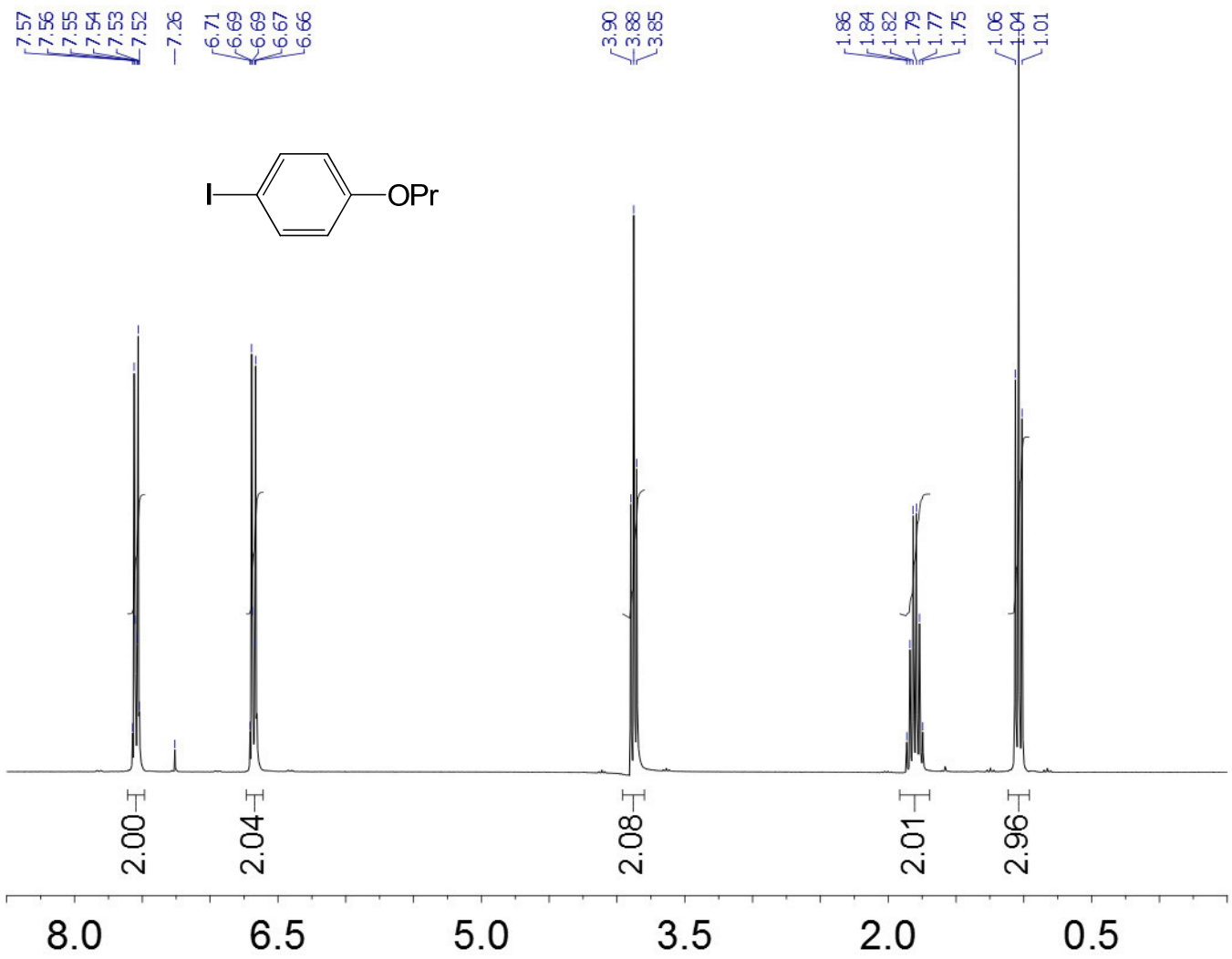

Figure B44. ^{1}HNMR ($CDCl_3$, 300 MHz) of **4-Propyloxy-iodobenzene, IV-1a**.

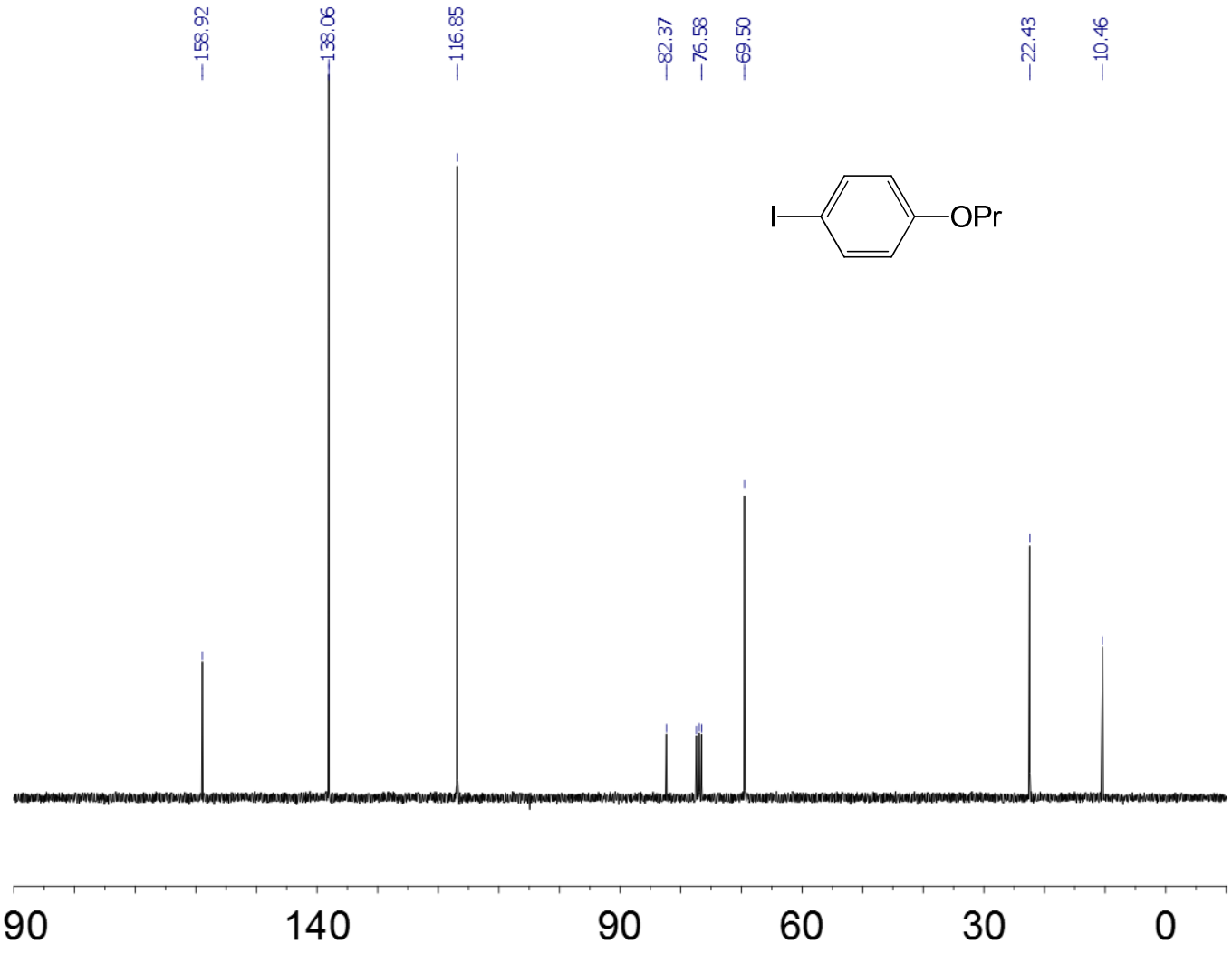

Figure B45. ^{13}CNMR ($CDCl_3$, 300 MHz) of **4-Propyloxy-iodobenzene, IV-1a**.

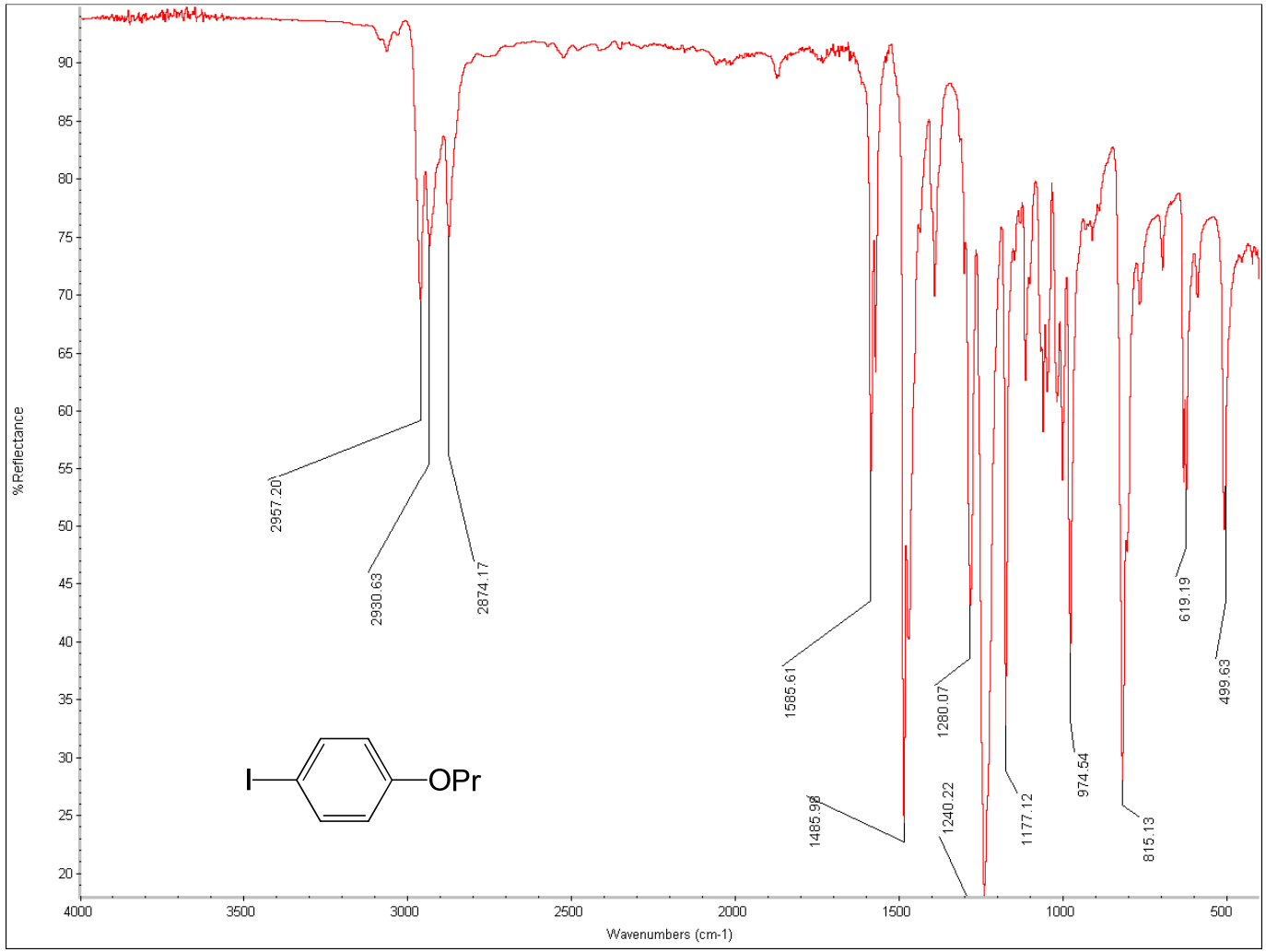

Figure B46. IR (ATIR, neat) of **4-Propyloxy-iodobenzene, IV-1a**.

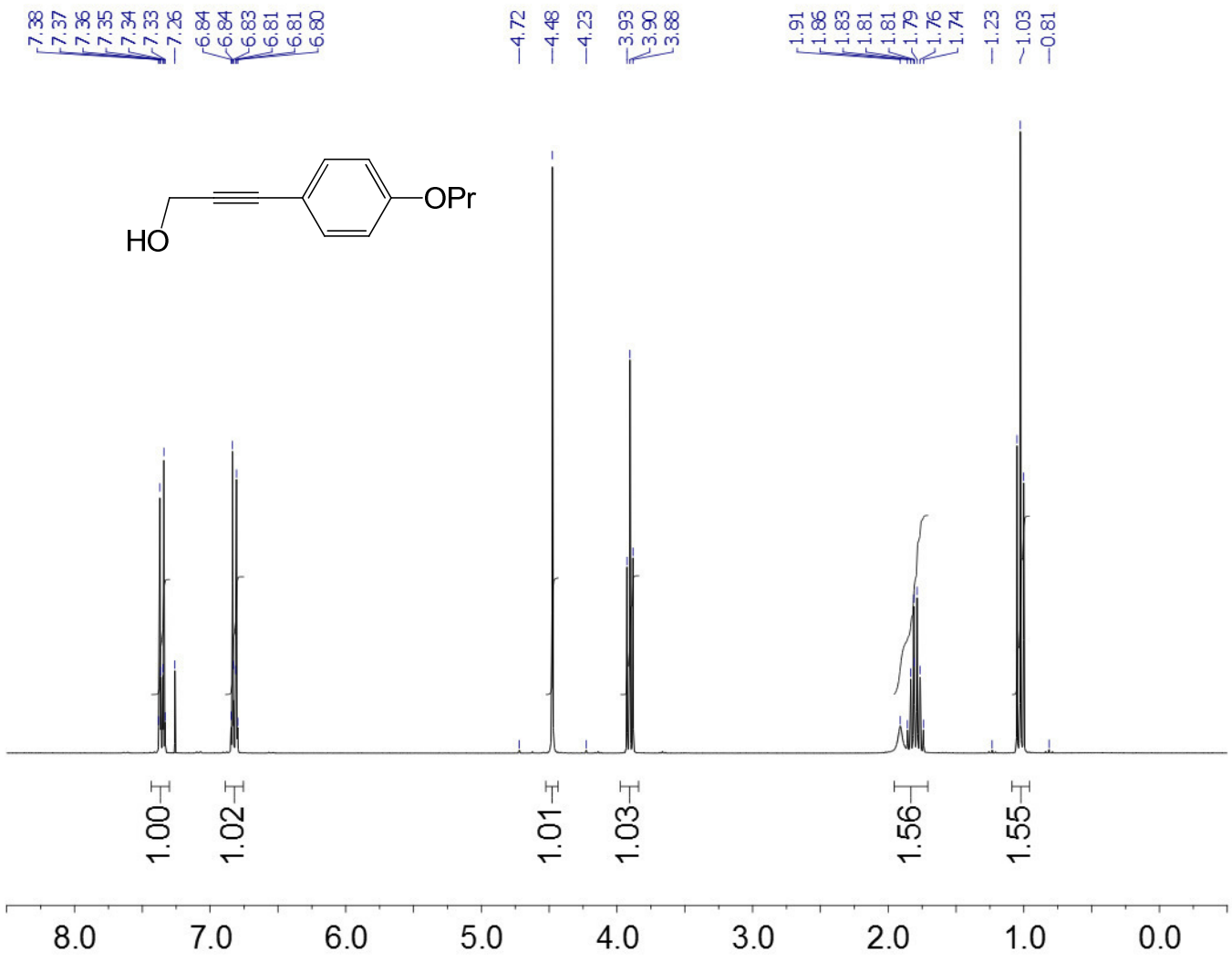

Figure B47. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1-(4-Propyloxyphenyl)propyn-3-ol, IV-1b**.

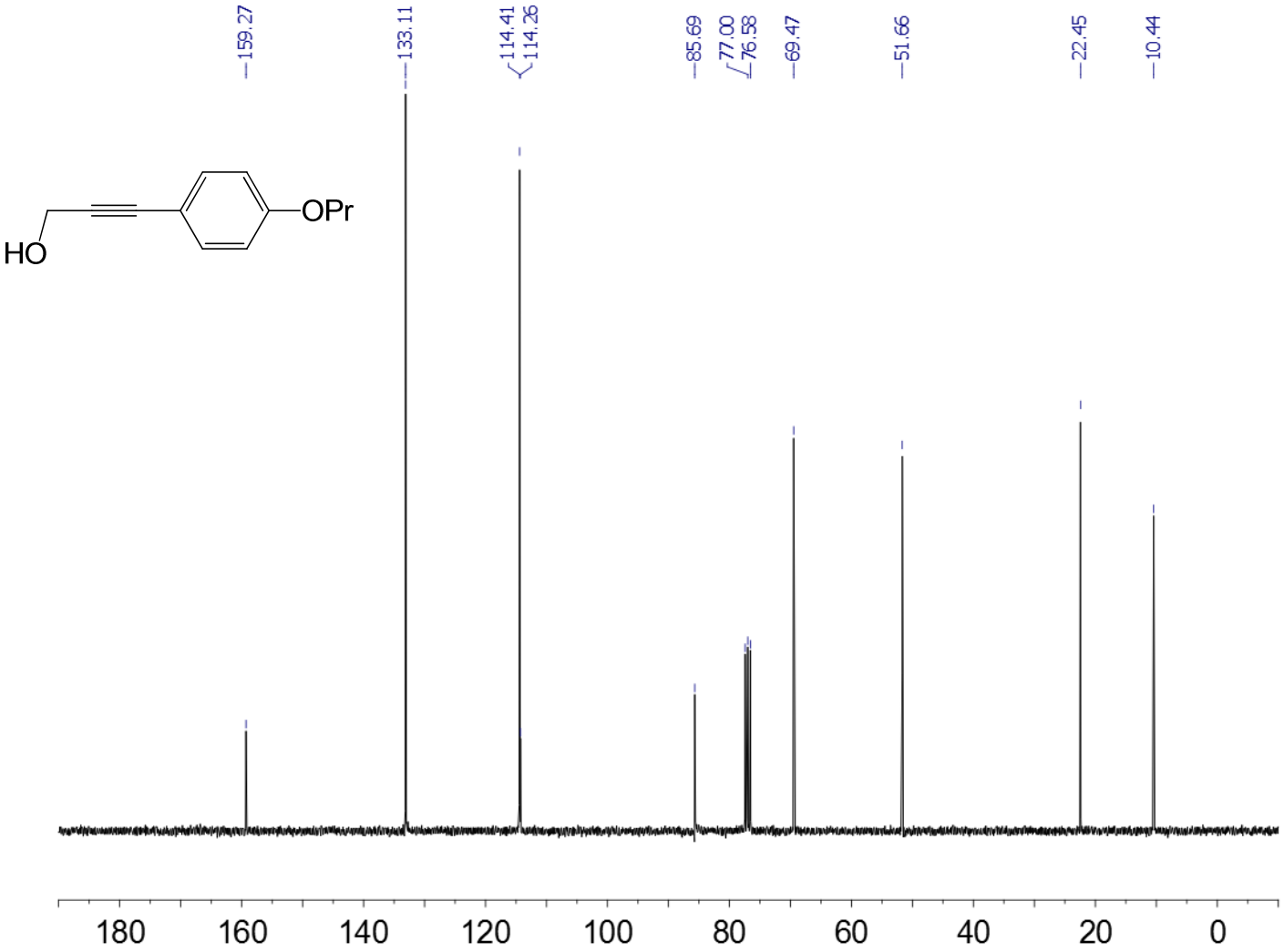

Figure B48. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1-(4-Propyloxyphenyl)propyn-3-ol, IV-1b**.

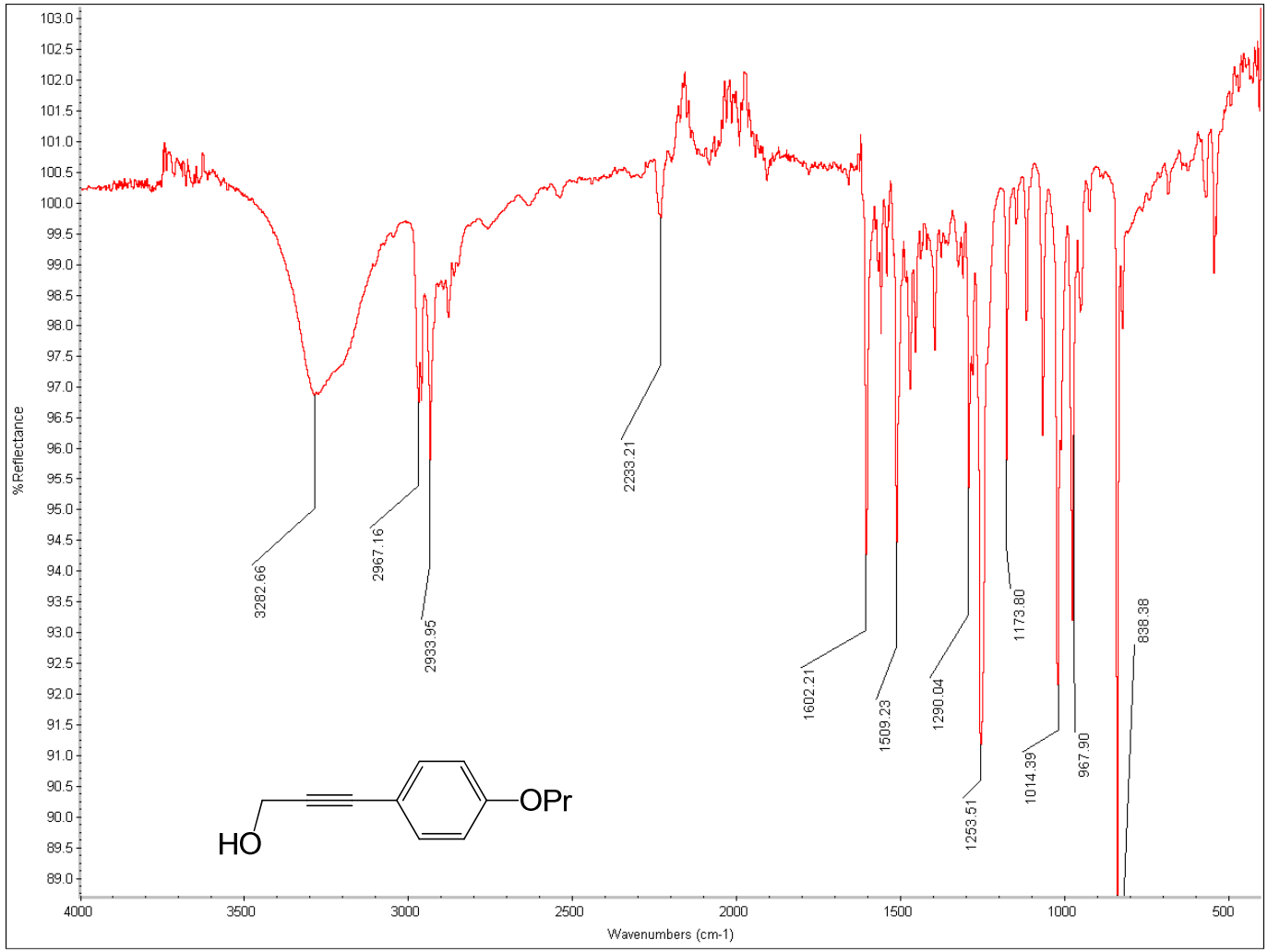

Figure B49. IR (ATIR, neat) of **1-(4-Propyloxyphenyl)propyn-3-ol, IV-1b**.

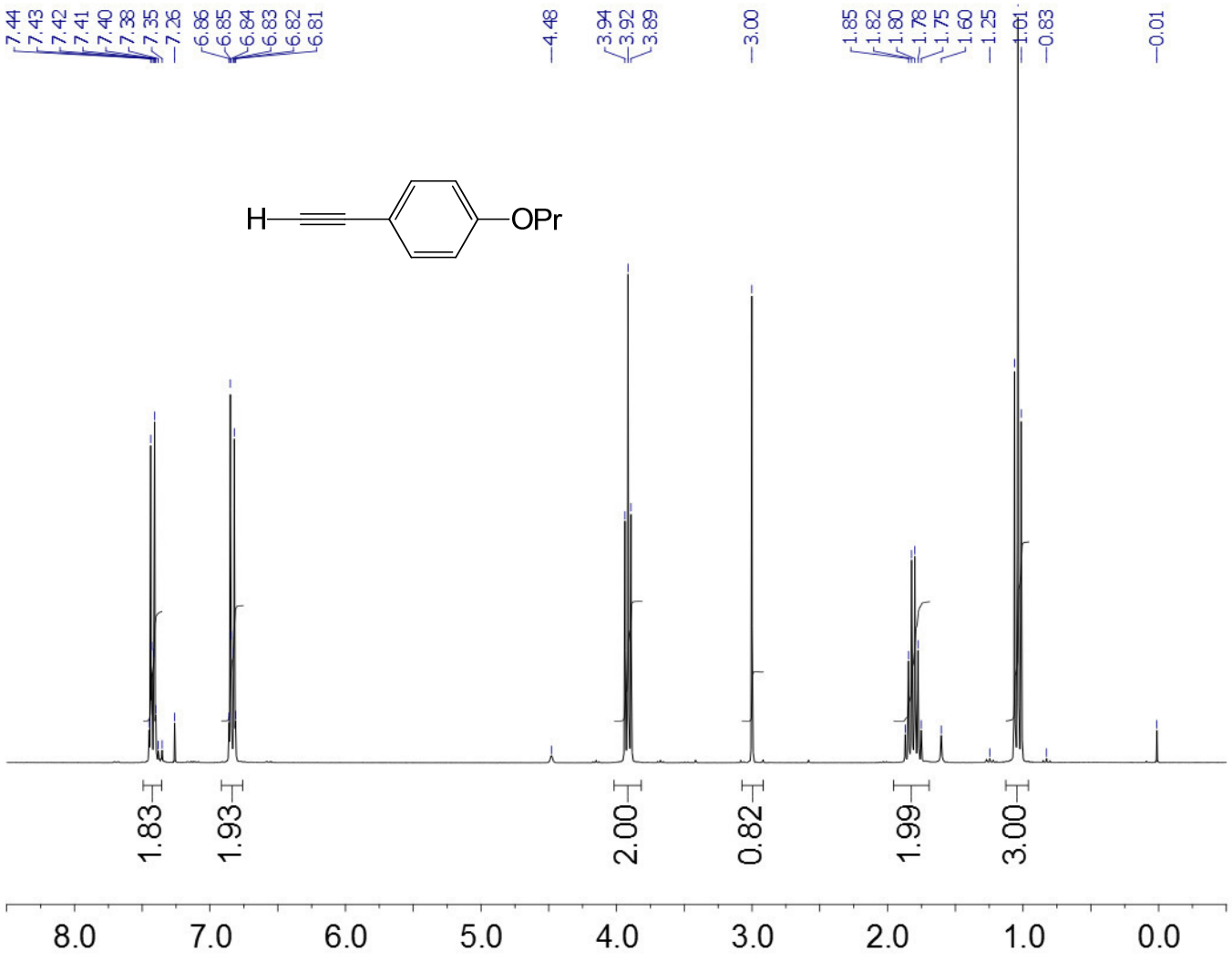

Figure B50. ^{1}HNMR ($CDCl_3$, 300 MHz) of **(4-Propyloxyphenyl)acetylene, IV-2**.

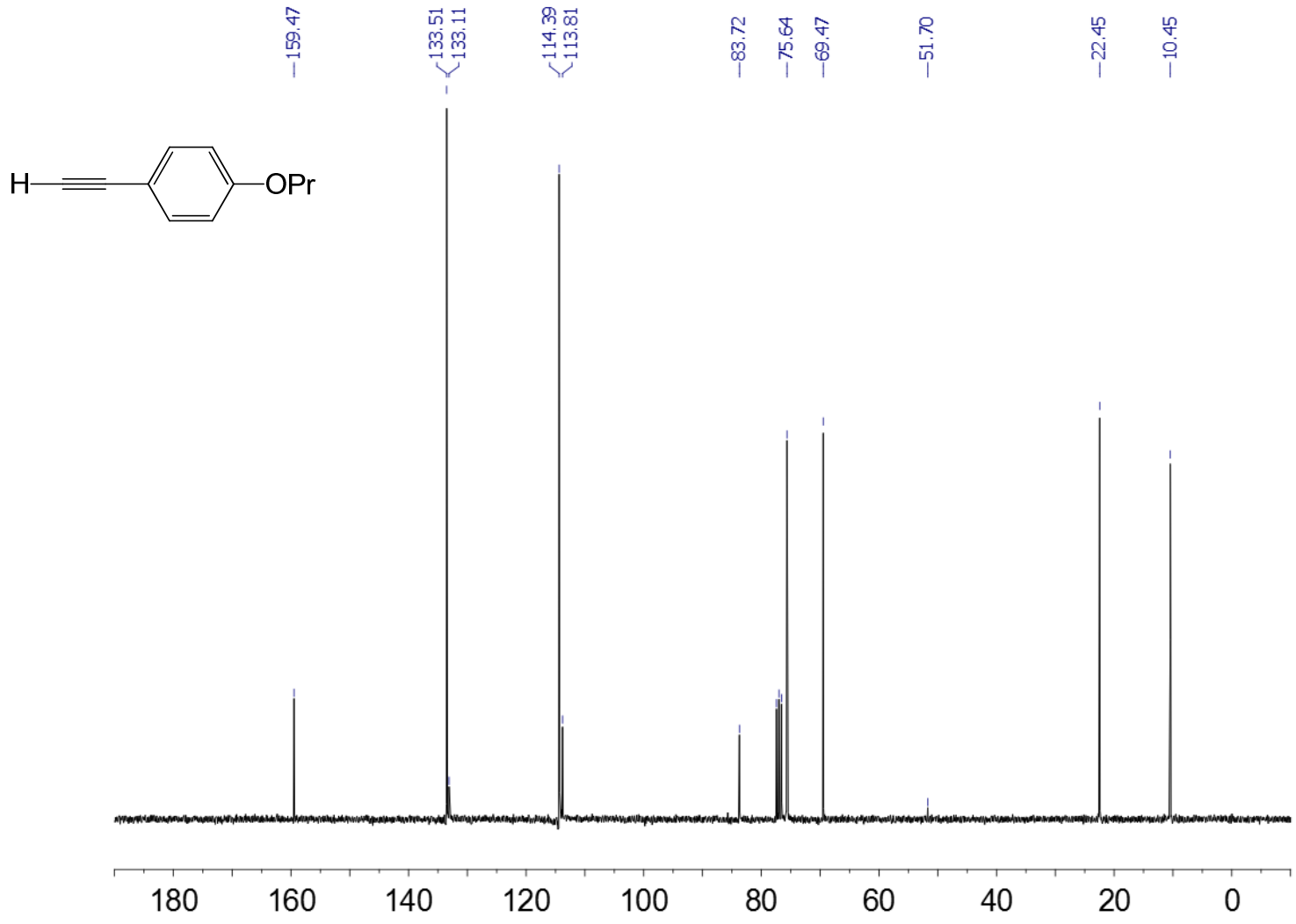

Figure B51. ^{13}CNMR ($CDCl_3$, 300 MHz) of **(4-Propyloxyphenyl)acetylene, IV-2**.

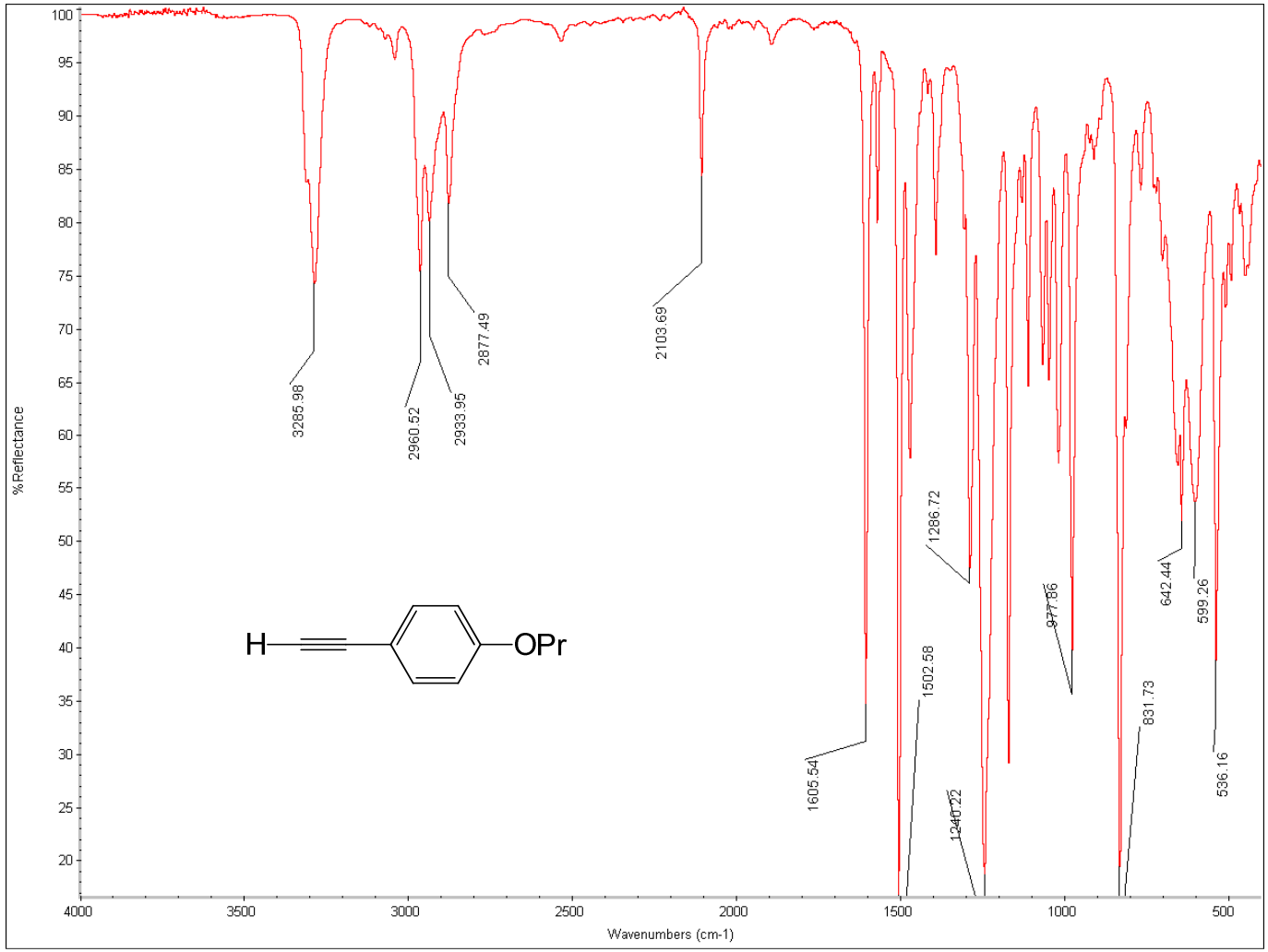

Figure B52. IR (ATIR, neat) of **(4-Propyloxyphenyl)acetylene, IV-2**.

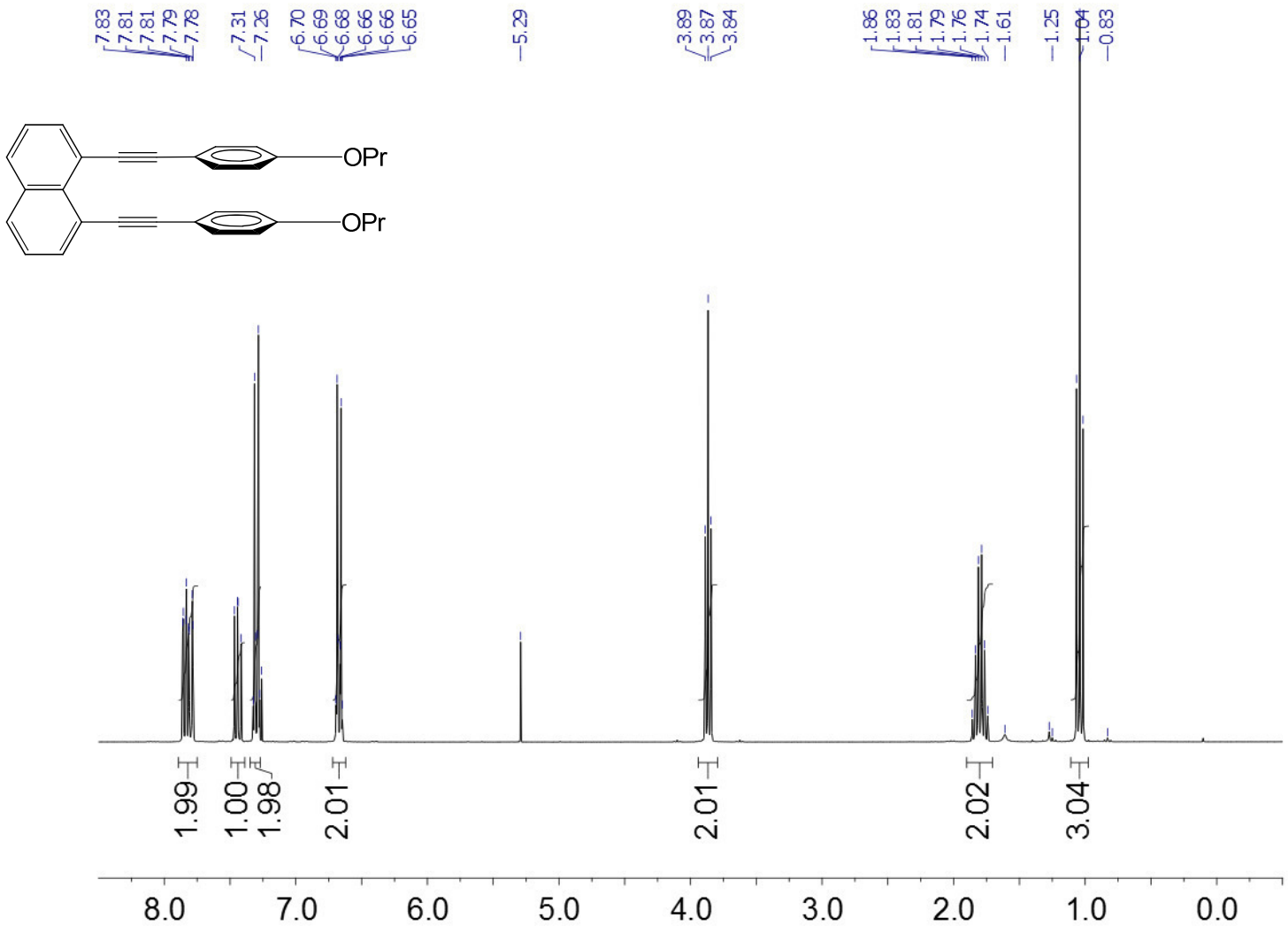

Figure B53. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1,8-(4-Propyloxyphenylethynyl)naphthalene, IV-3**.

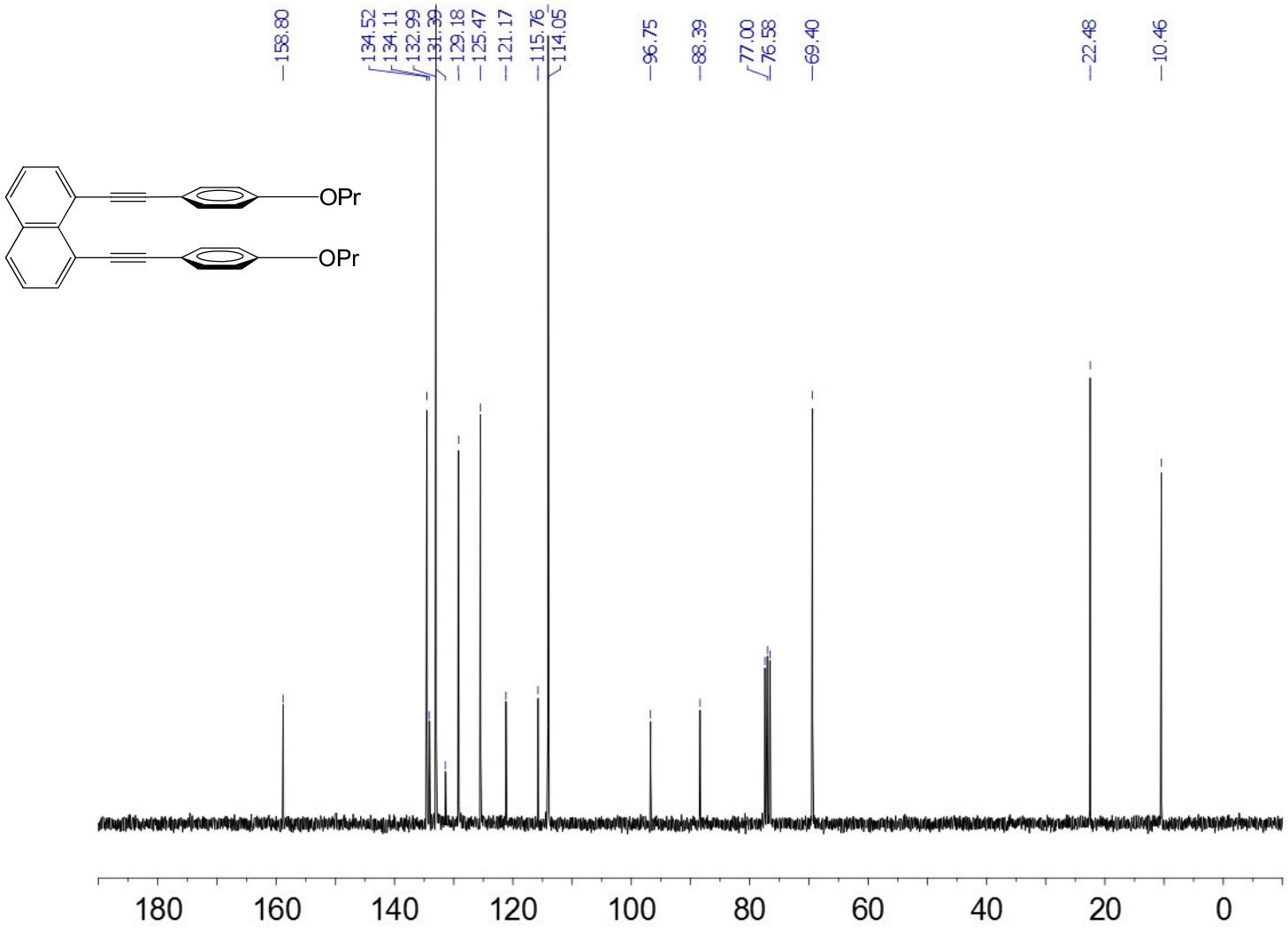

Figure B54. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1,8-(4-Propyloxyphenylethynyl)naphthalene, IV-3**.

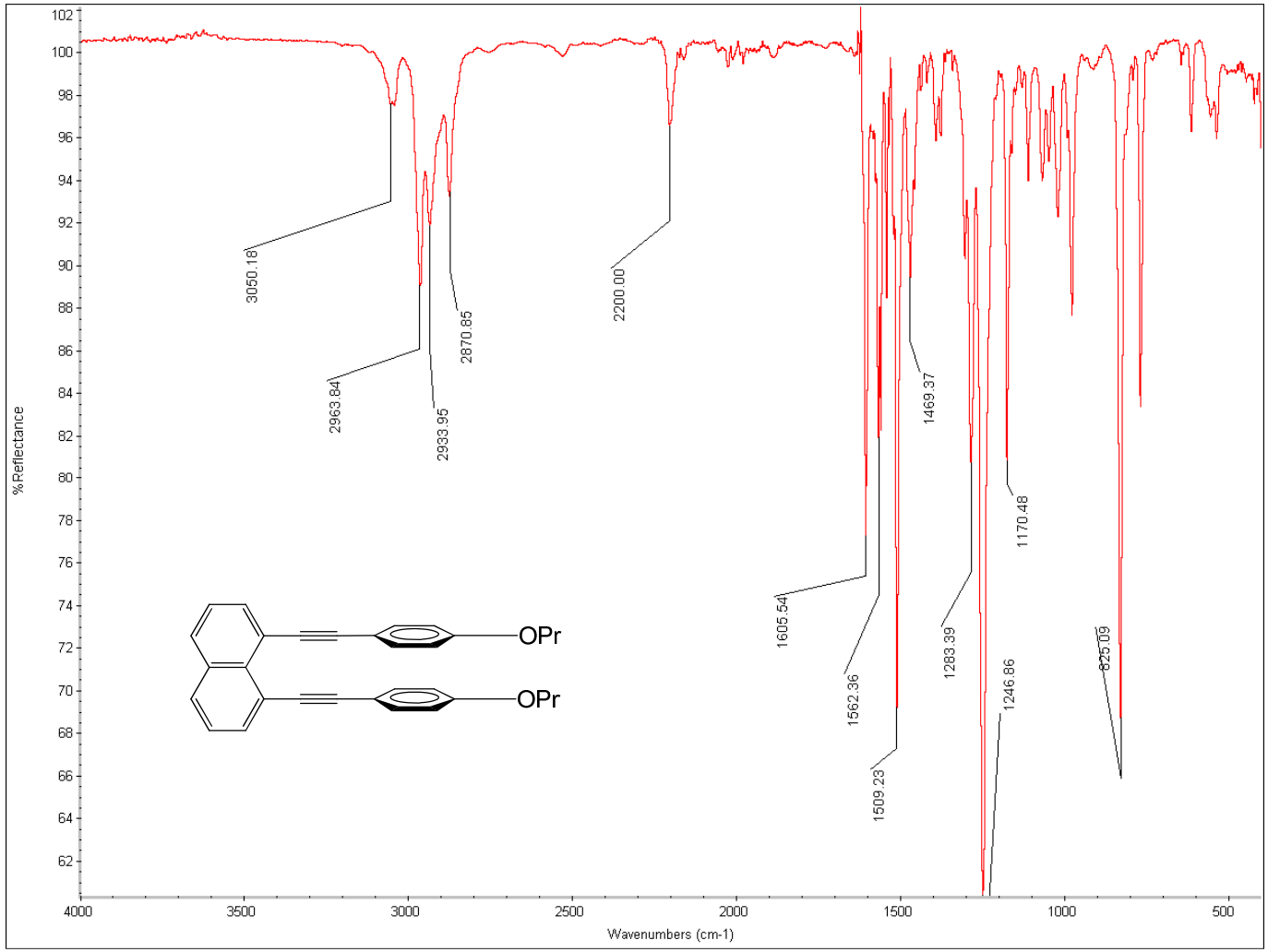

Figure B55. IR (ATIR, neat) of **1,8-(4-Propyloxyphenylethynyl)naphthalene, IV-3**.

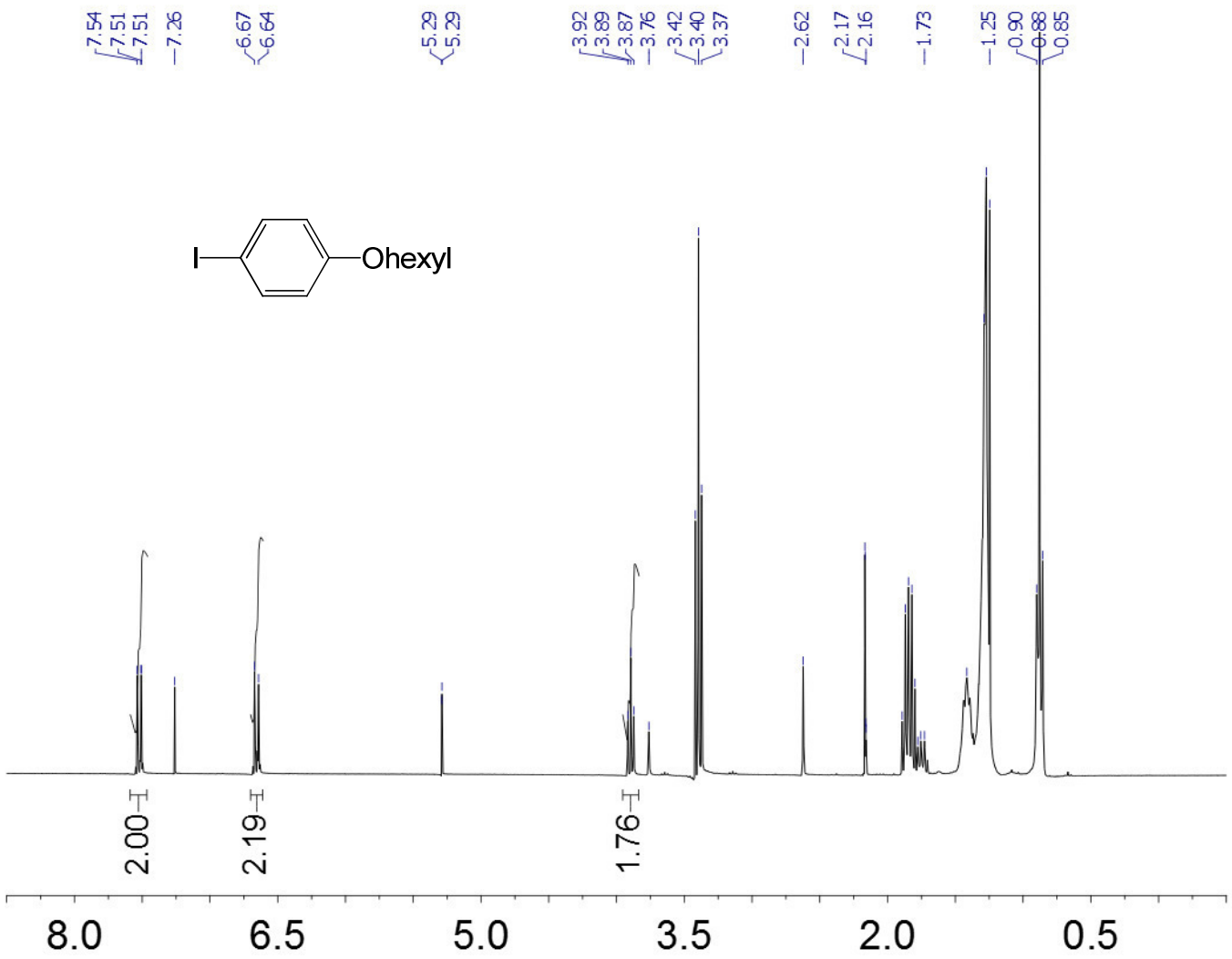

Figure B56. ^{1}HNMR ($CDCl_3$, 300 MHz) of **4-Hexyloxy-1-iodobenzene, IV-4a**.

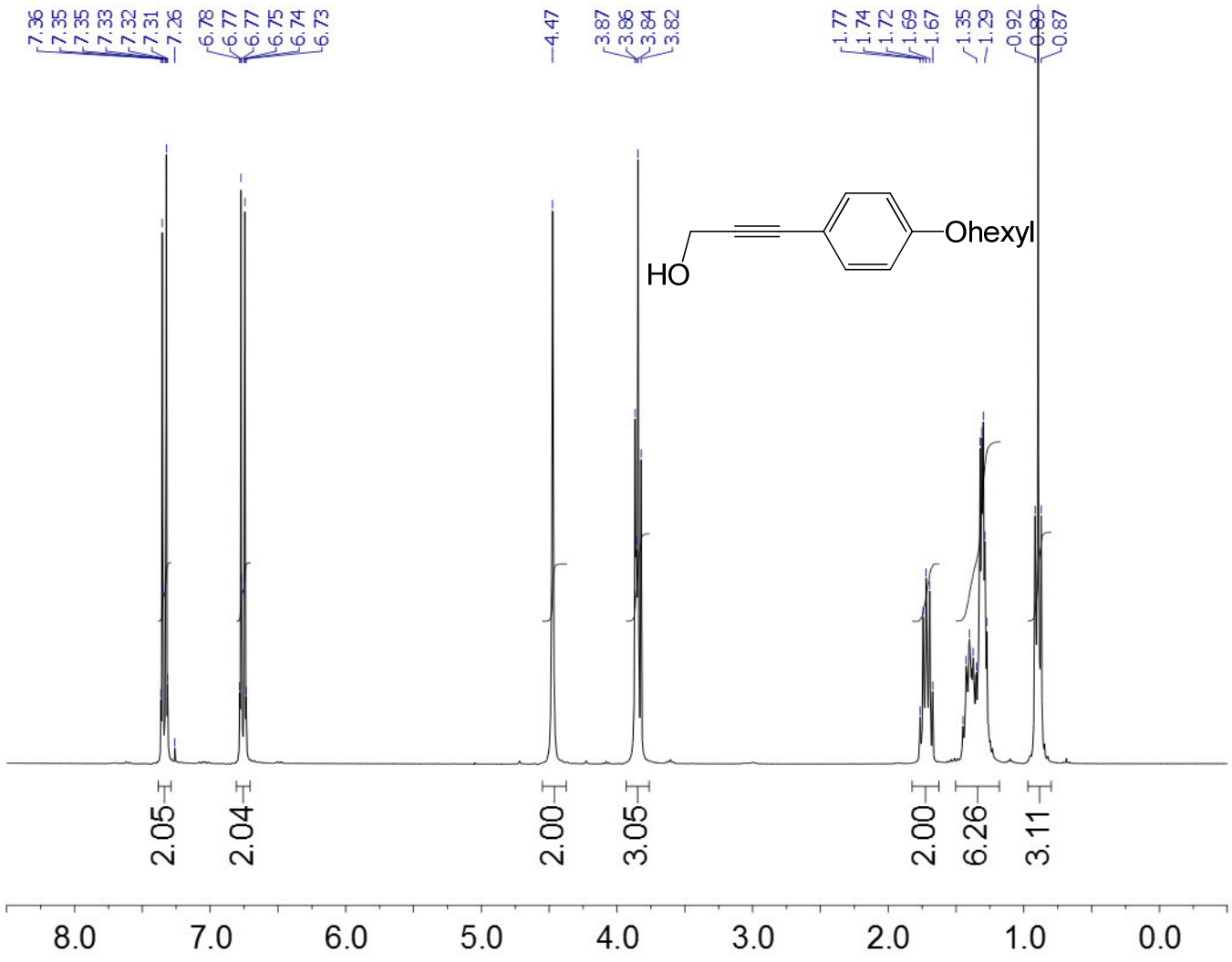

Figure B57. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1-(4-Hexyloxyphenyl)propyn-3-ol, IV-4b**.

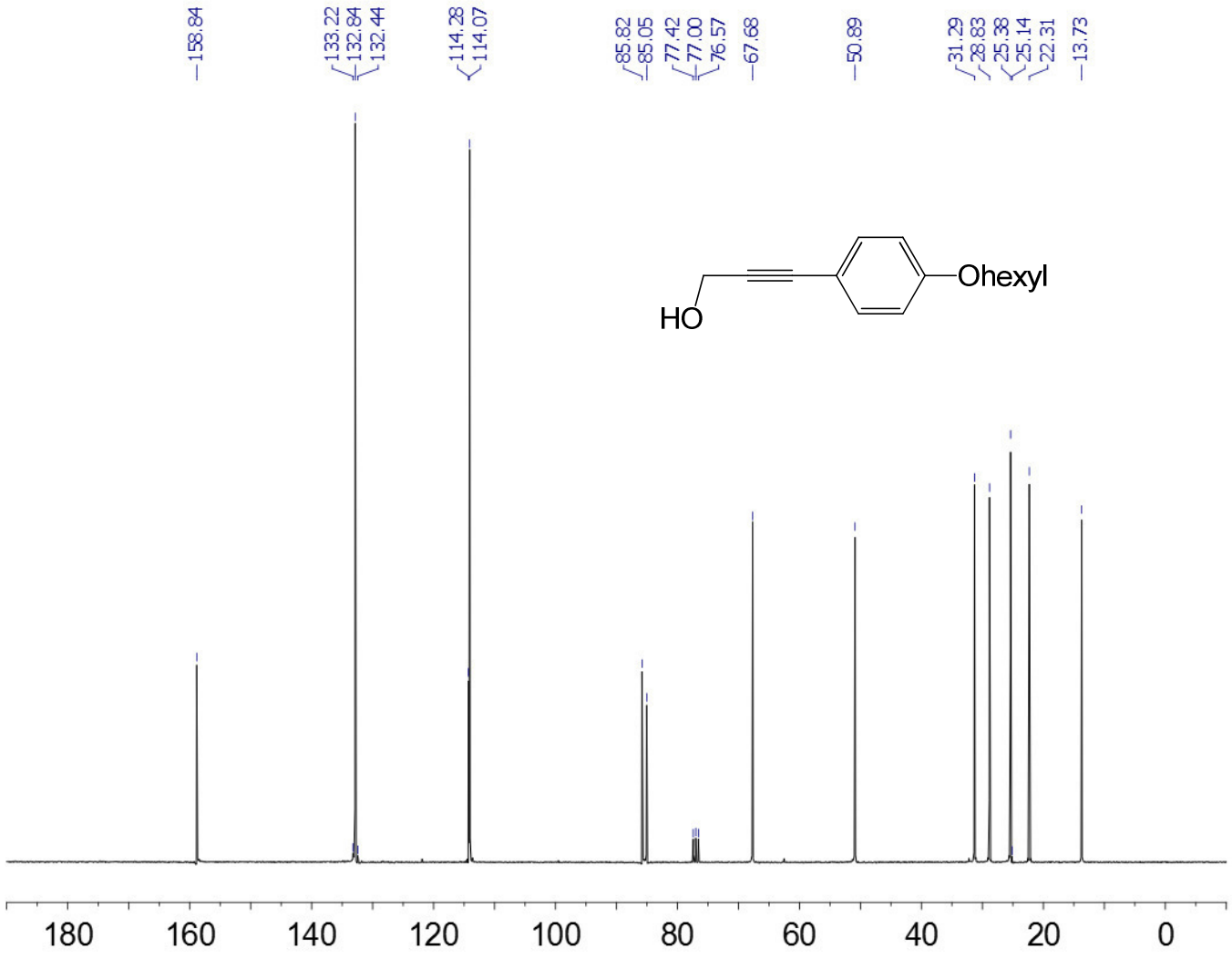

Figure B58. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1-(4-Hexyloxyphenyl)propyn-3-ol, IV-4b**.

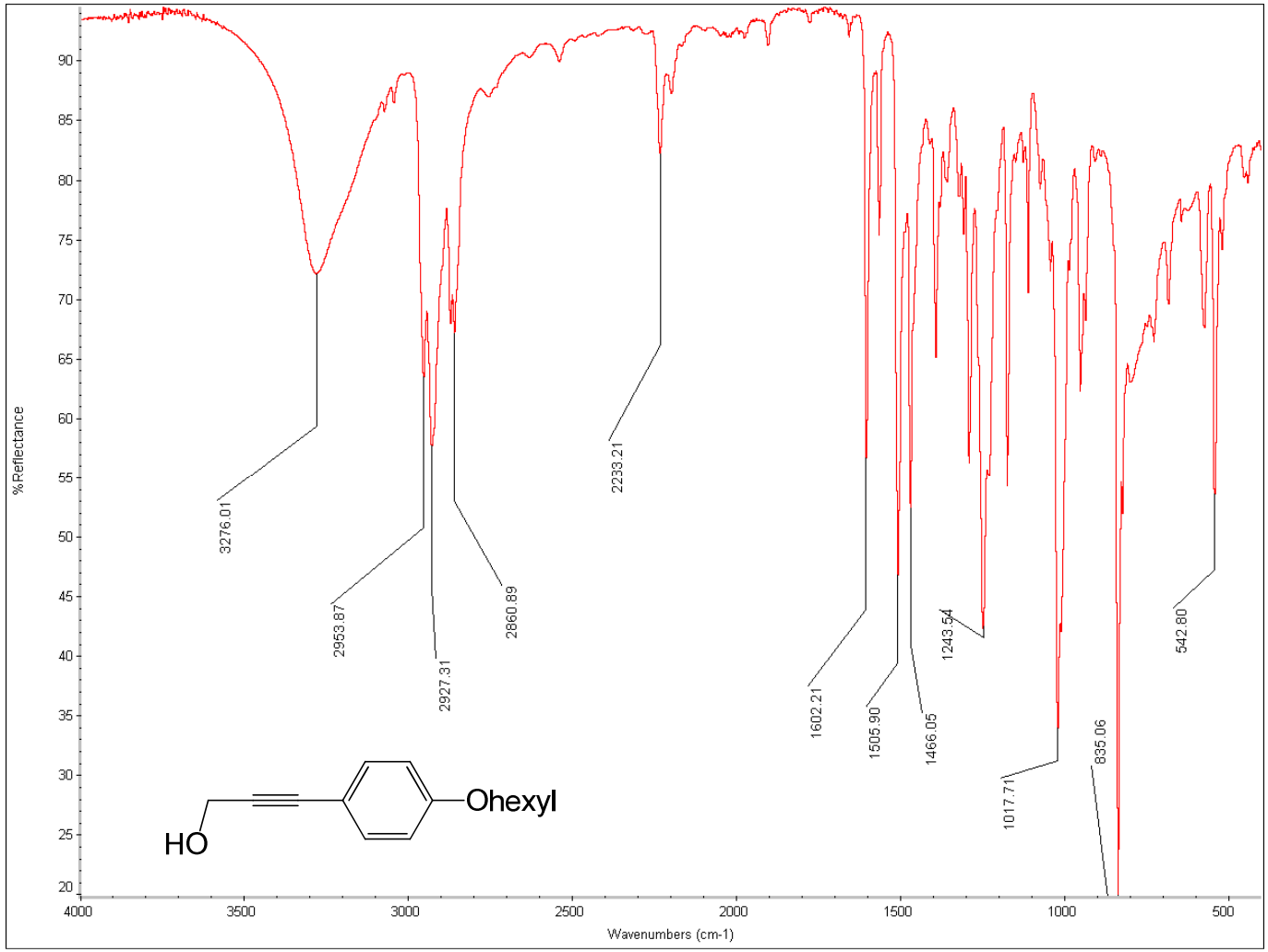

Figure B59. IR (ATIR, neat) of **1-(4-Hexyloxyphenyl)propyn-3-ol, IV-4b**.

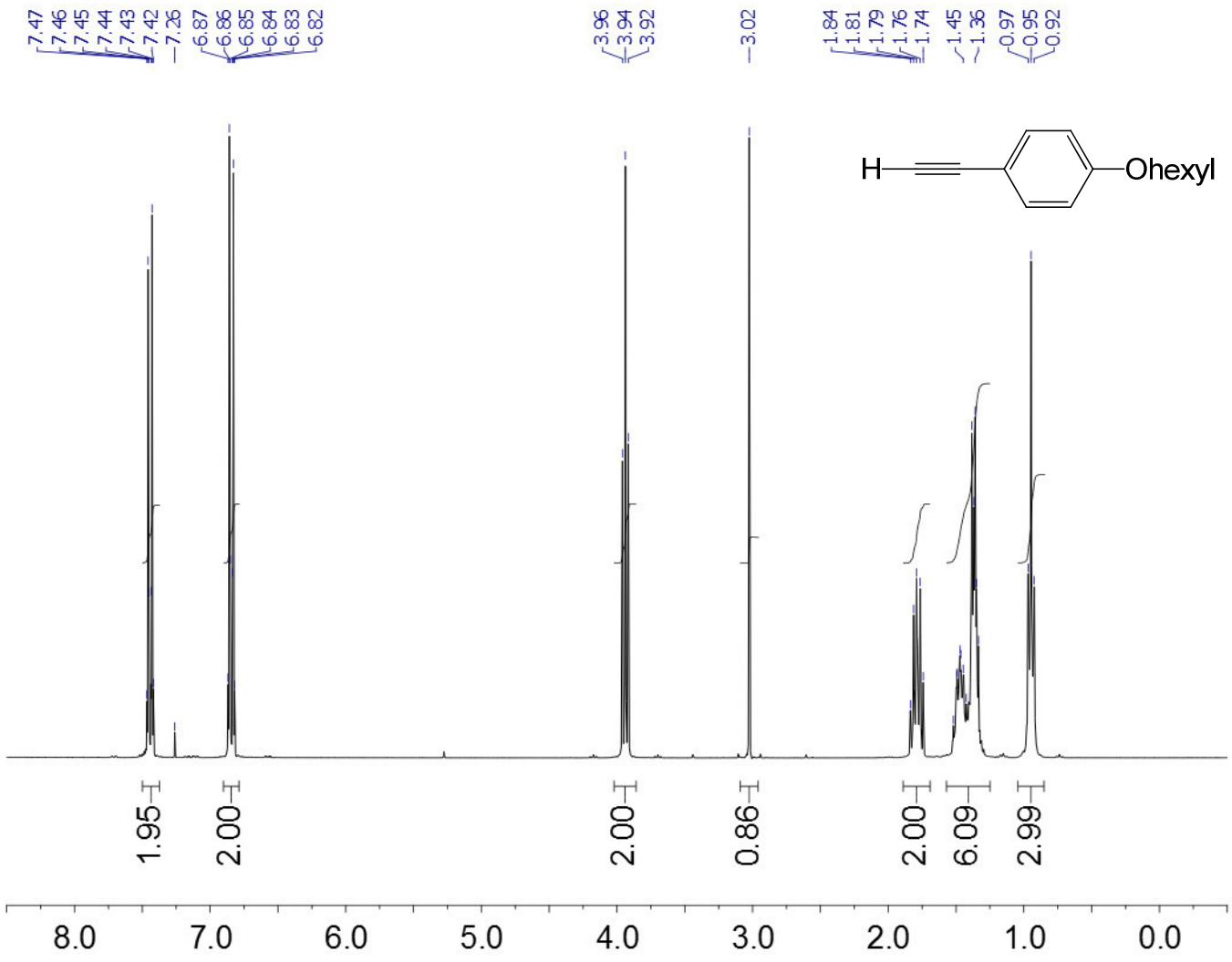

Figure B60. ^{1}HNMR ($CDCl_3$, 300 MHz) of **(4-Hexyloxyphenyl)acetylene, IV-5**.

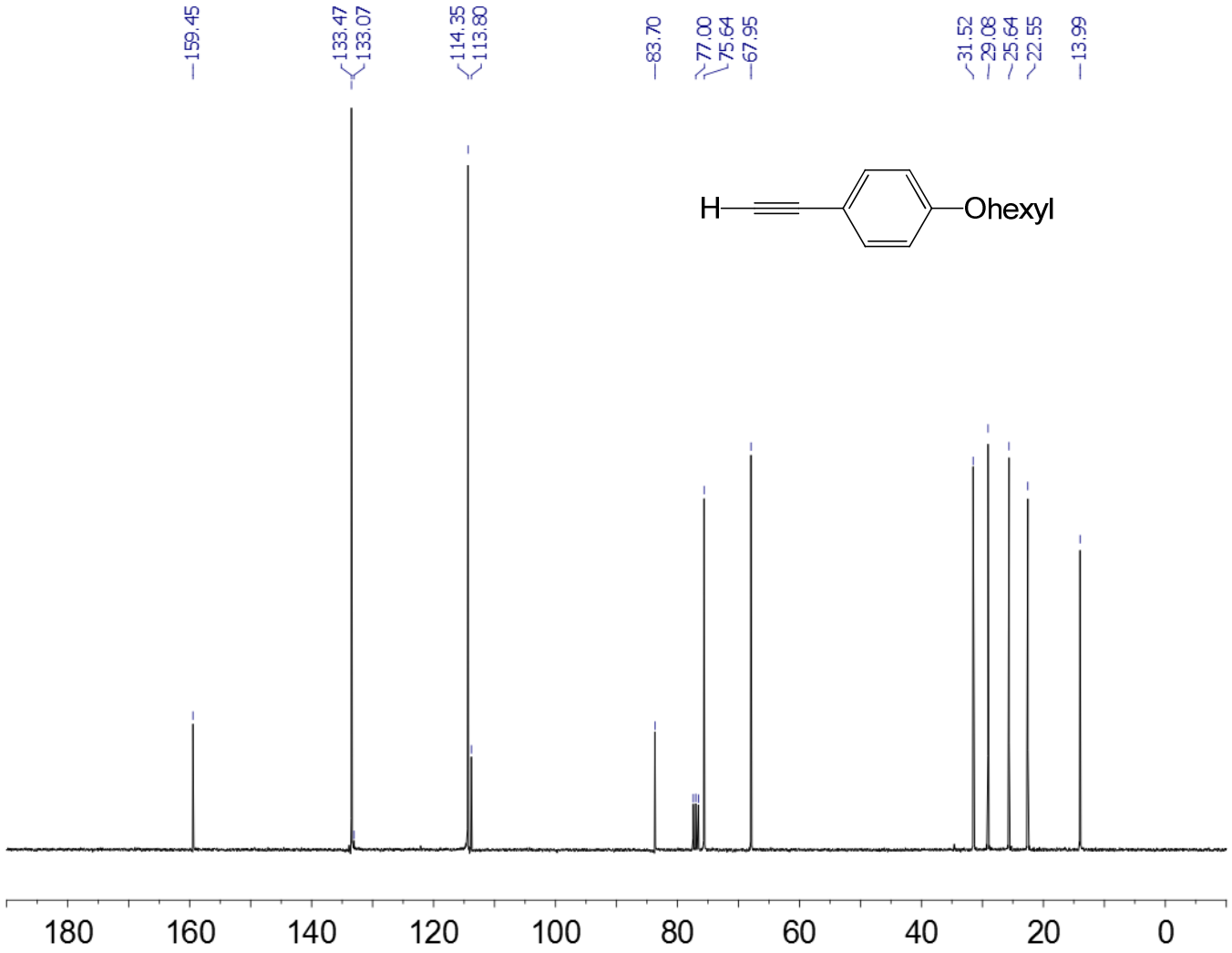

Figure B61. ^{13}CNMR ($CDCl_3$, 300 MHz) of **(4-Hexyloxyphenyl)acetylene, IV-5**.

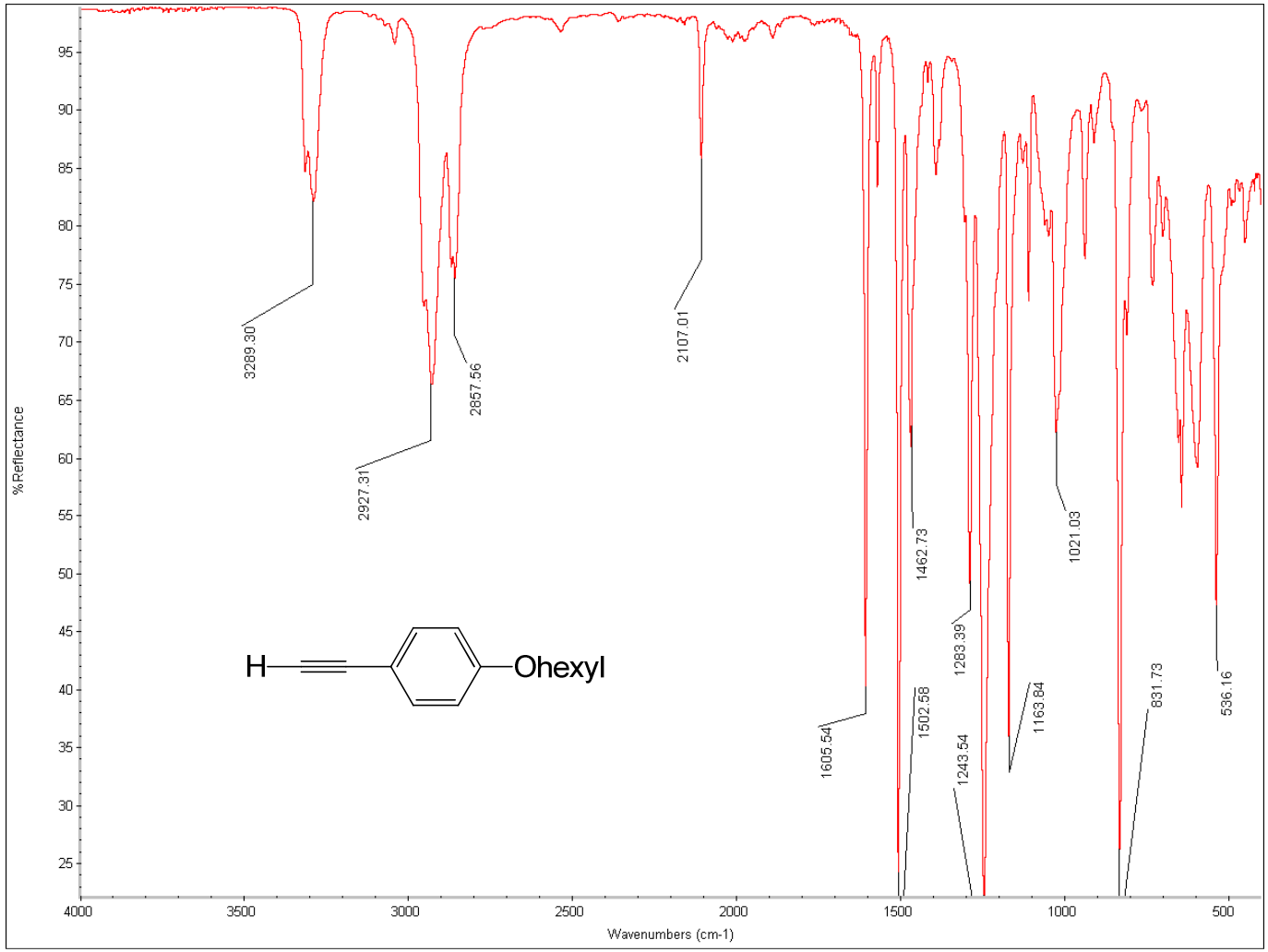

Figure B62. IR (ATIR, neat) of **(4-Hexyloxyphenyl)acetylene, IV-5**.

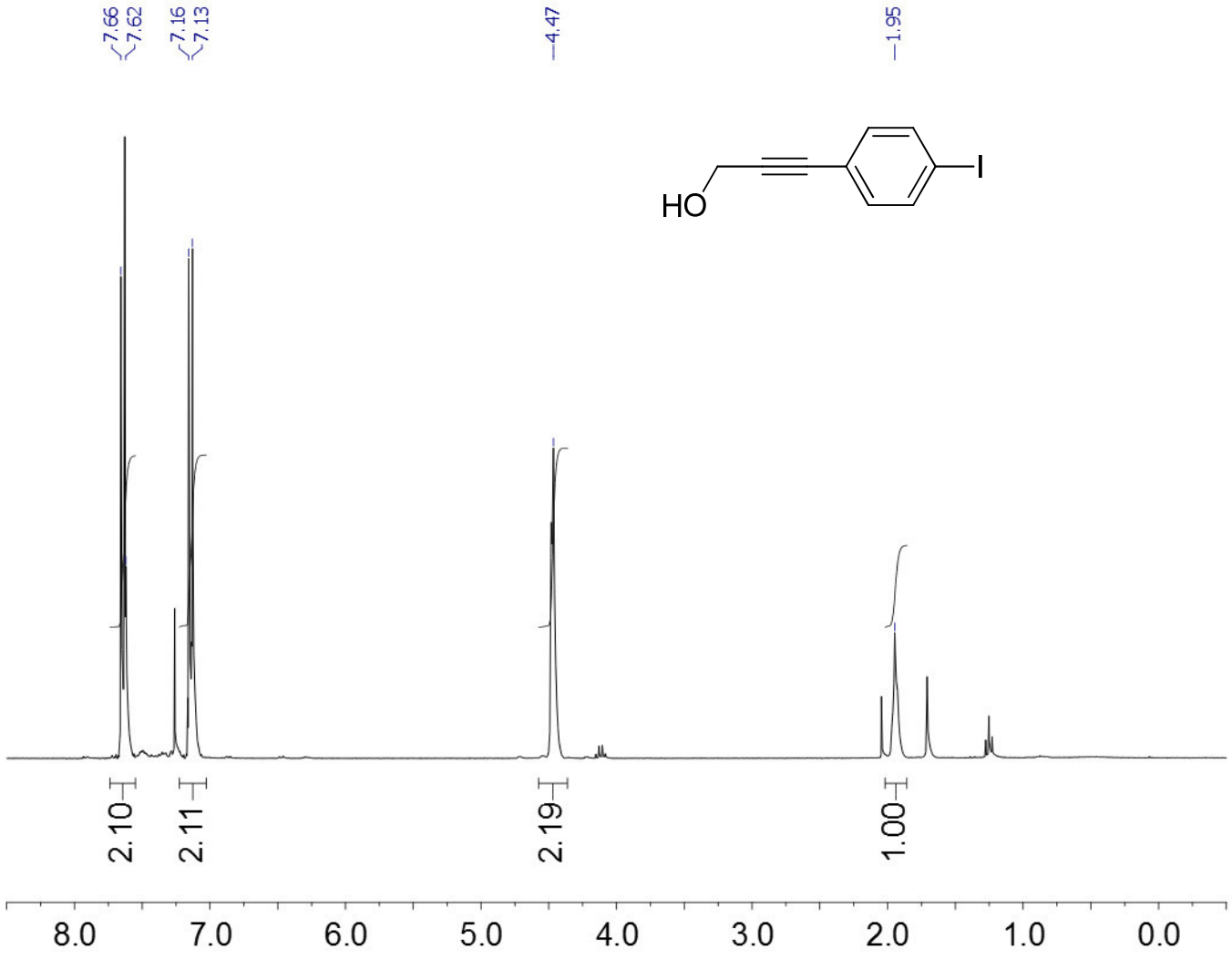

Figure B63. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1-(4-Iodophenyl)propyn-3-ol, IV-6**.

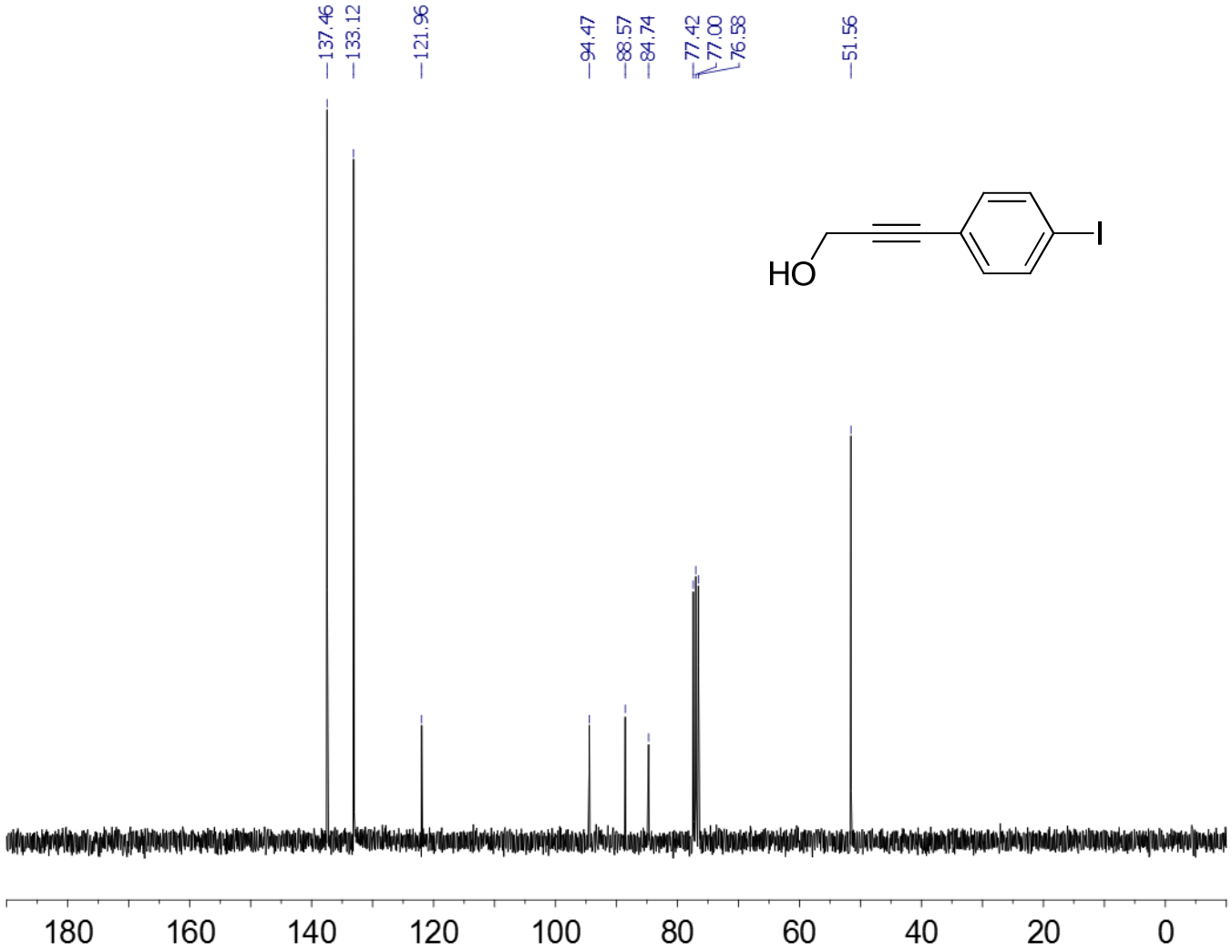

Figure B64. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1-(4-Iodophenyl)propyn-3-ol, IV-6**.

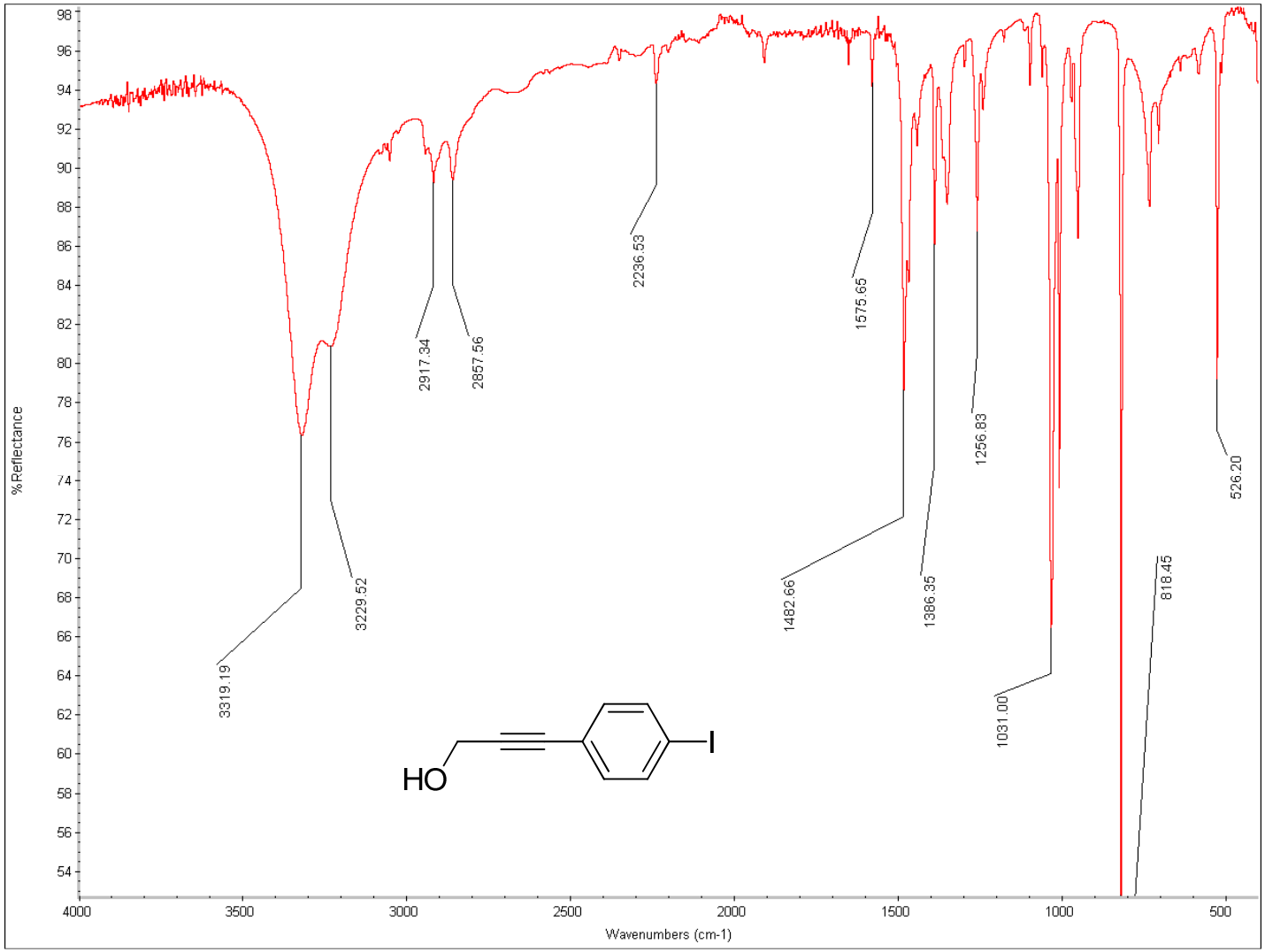

Figure B65. IR (ATIR, neat) of **1-(4-Iodophenyl)propyn-3-ol, IV-6**.

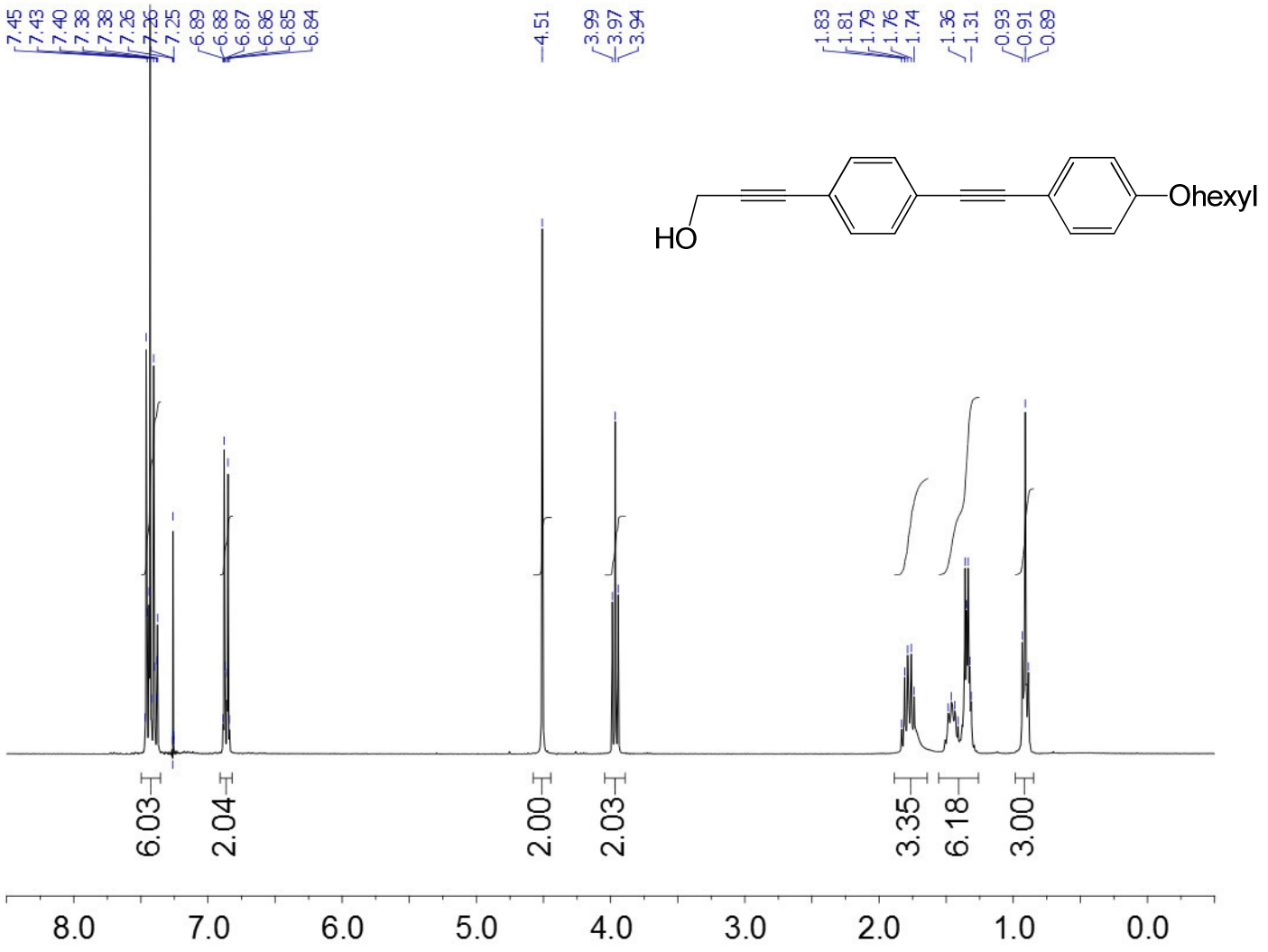

Figure B66. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1-(4-(4-Hexyloxyphenylethynylene)phenyl)propyn-3-ol, IV-7**.

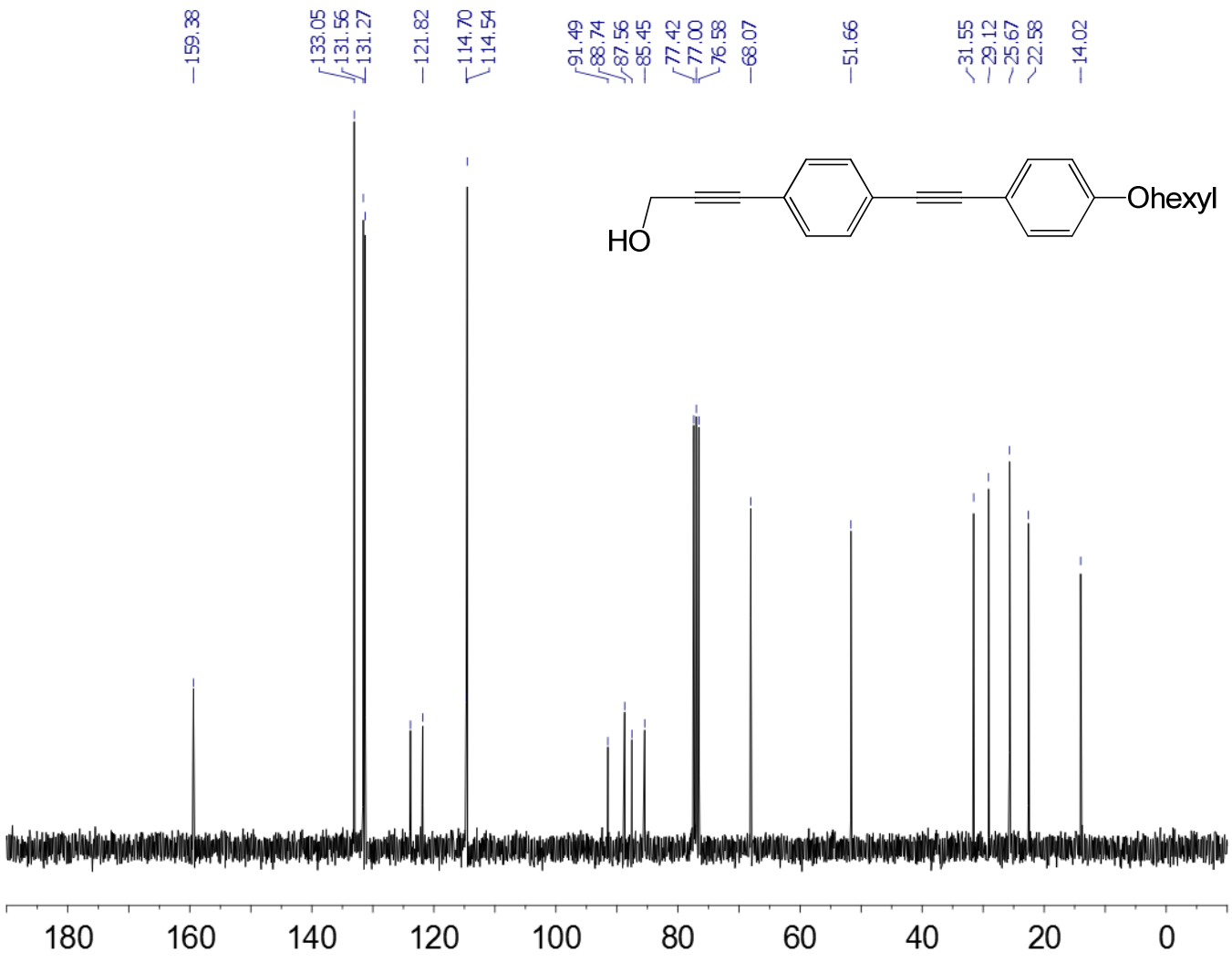

Figure B67. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1-(4-(4-Hexyloxyphenylethynylene)phenyl)propyn-3-ol, IV-7**.

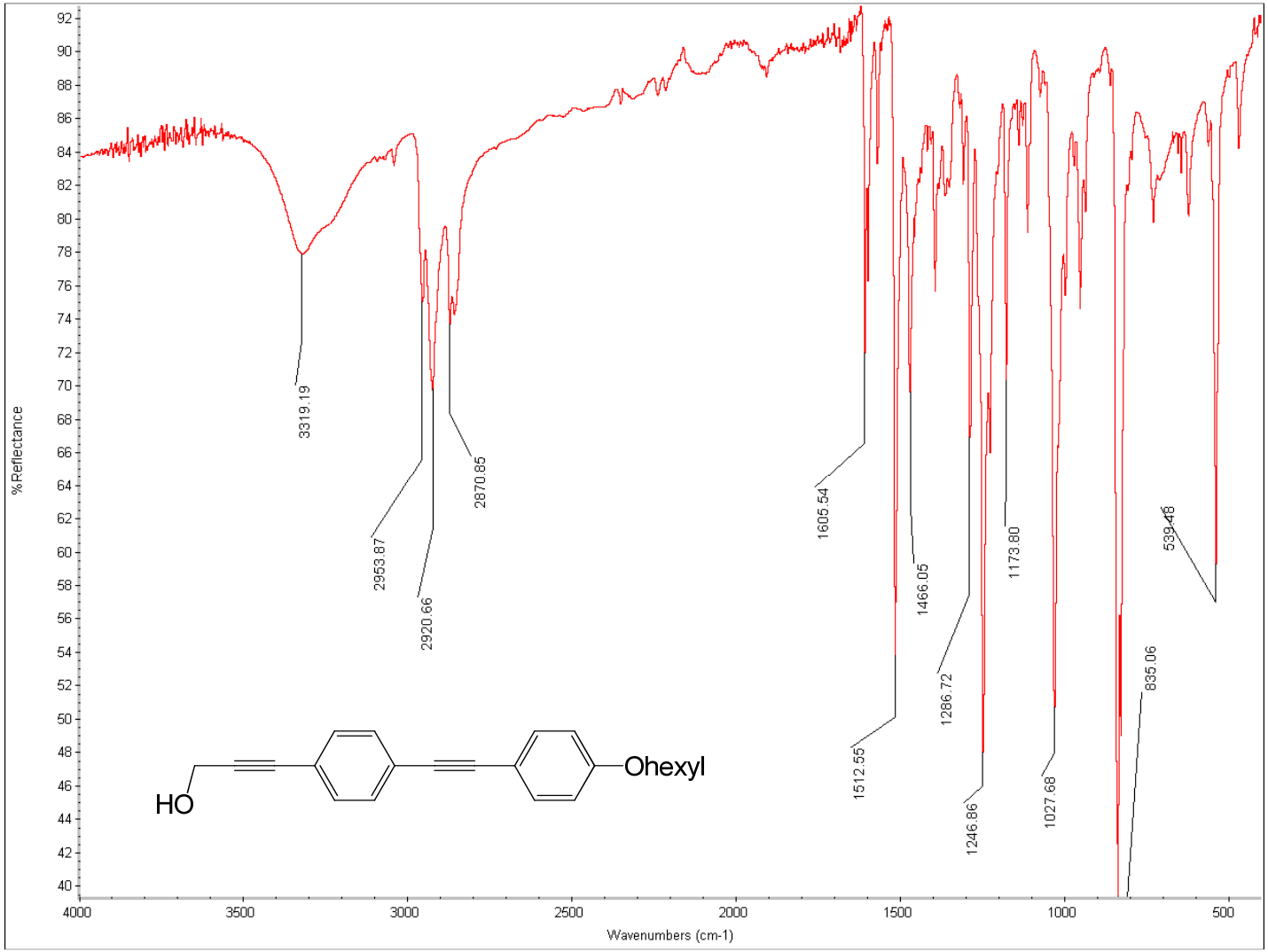

Figure B68. IR (ATIR, neat) of **1-(4-(4-Hexyloxyphenylethynylene)phenyl)propyn-3-ol, IV-7**.

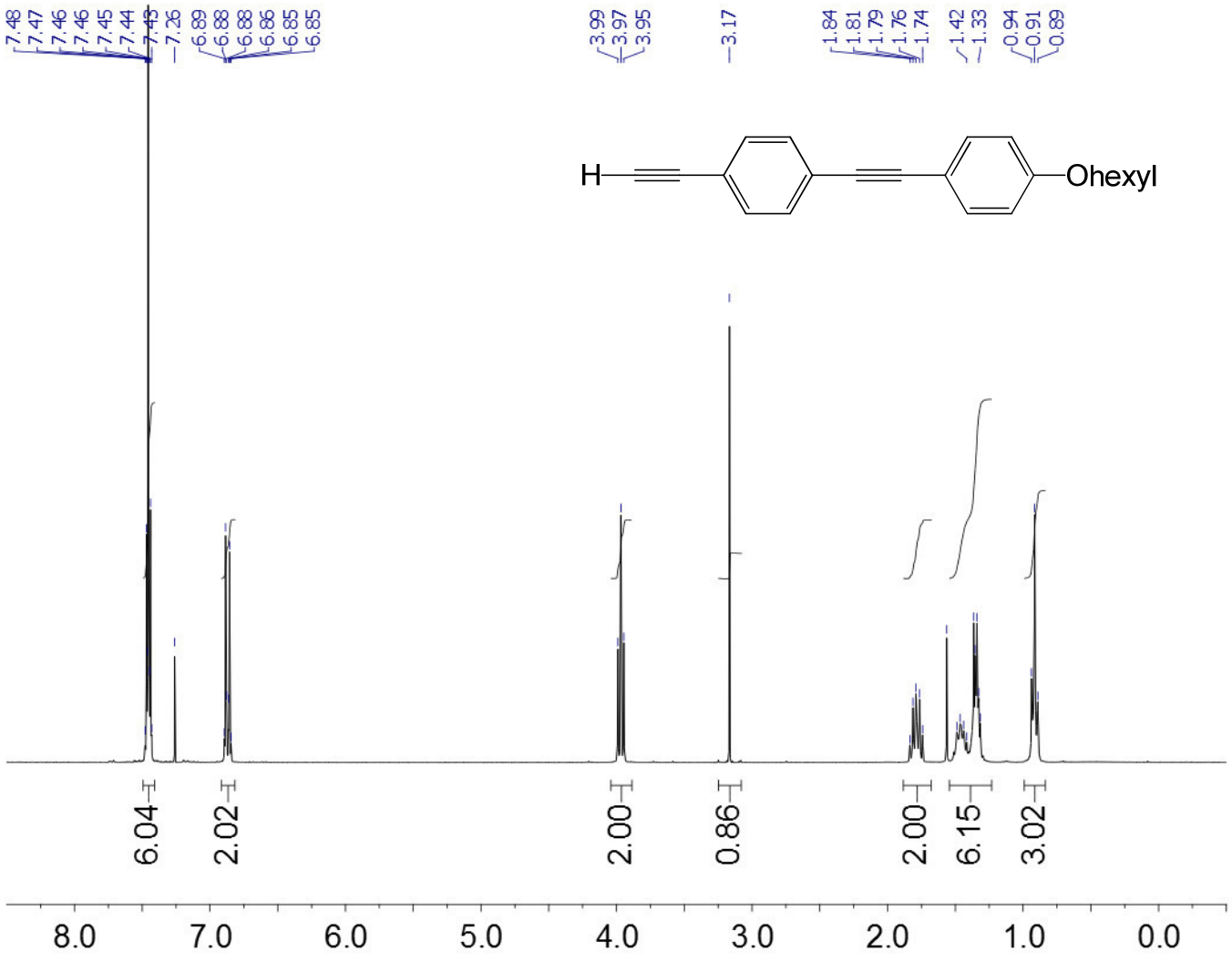

Figure B69. ^{1}HNMR ($CDCl_3$, 300 MHz) of **(4-(4-Hexyloxyphenylethynyl)phenyl)acetylene, IV-8**.

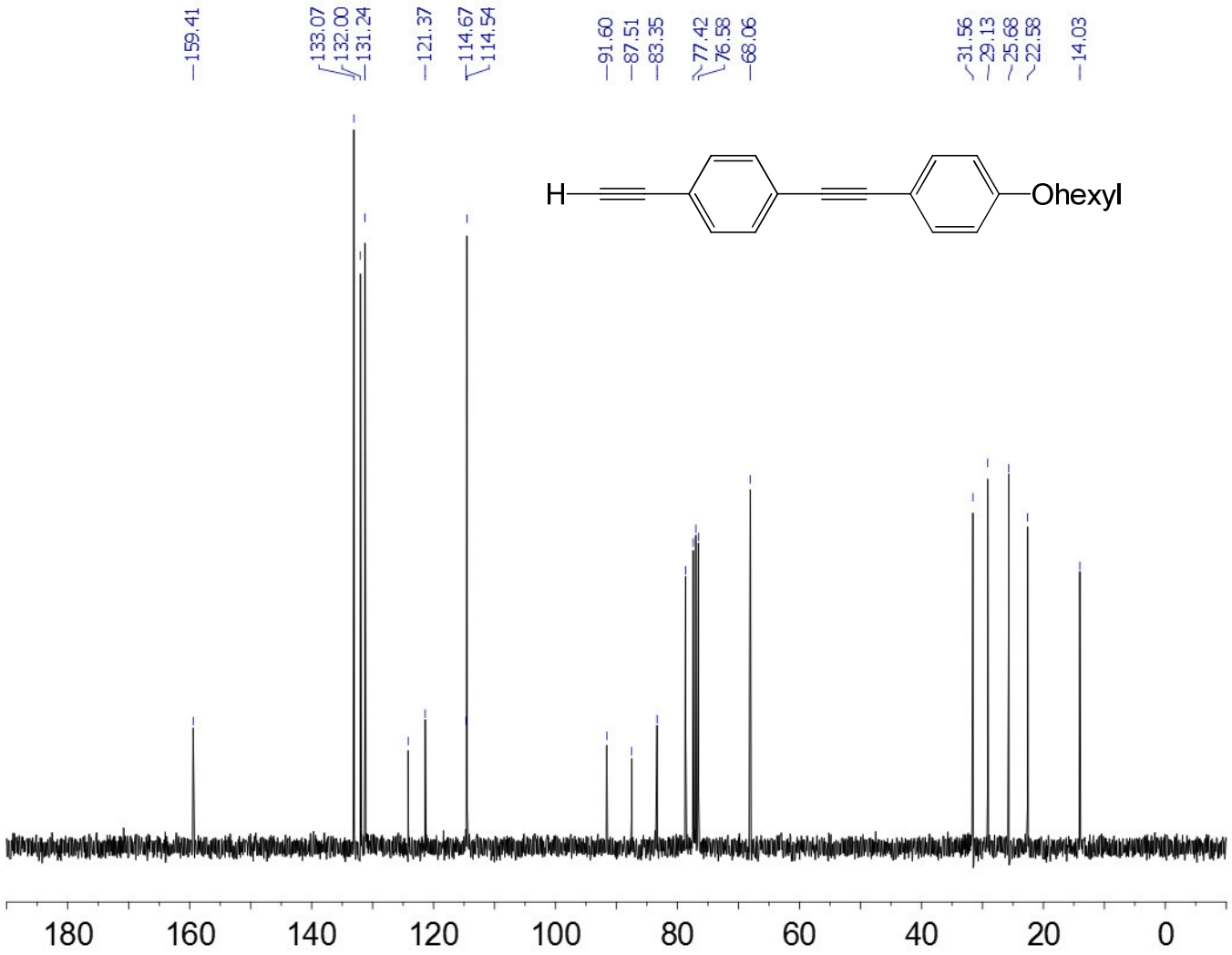

Figure B70. ^{13}CNMR ($CDCl_3$, 300 MHz) of **(4-(4-Hexyloxyphenylethynyl)phenyl)acetylene, IV-8**.

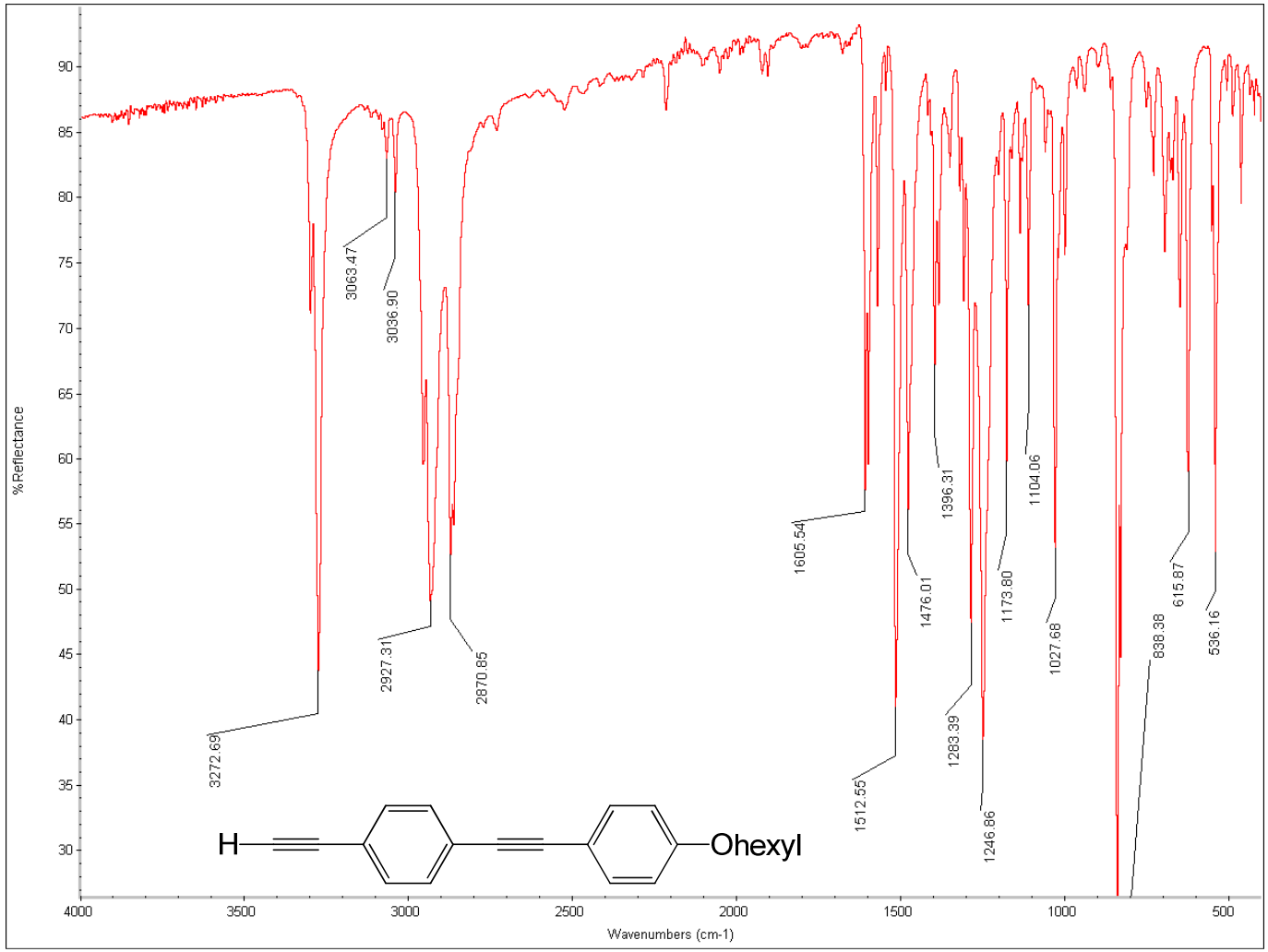

Figure B71. IR (ATIR, neat) of **(4-(4-Hexyloxyphenylethynyl)phenyl)acetylene, IV-8**.

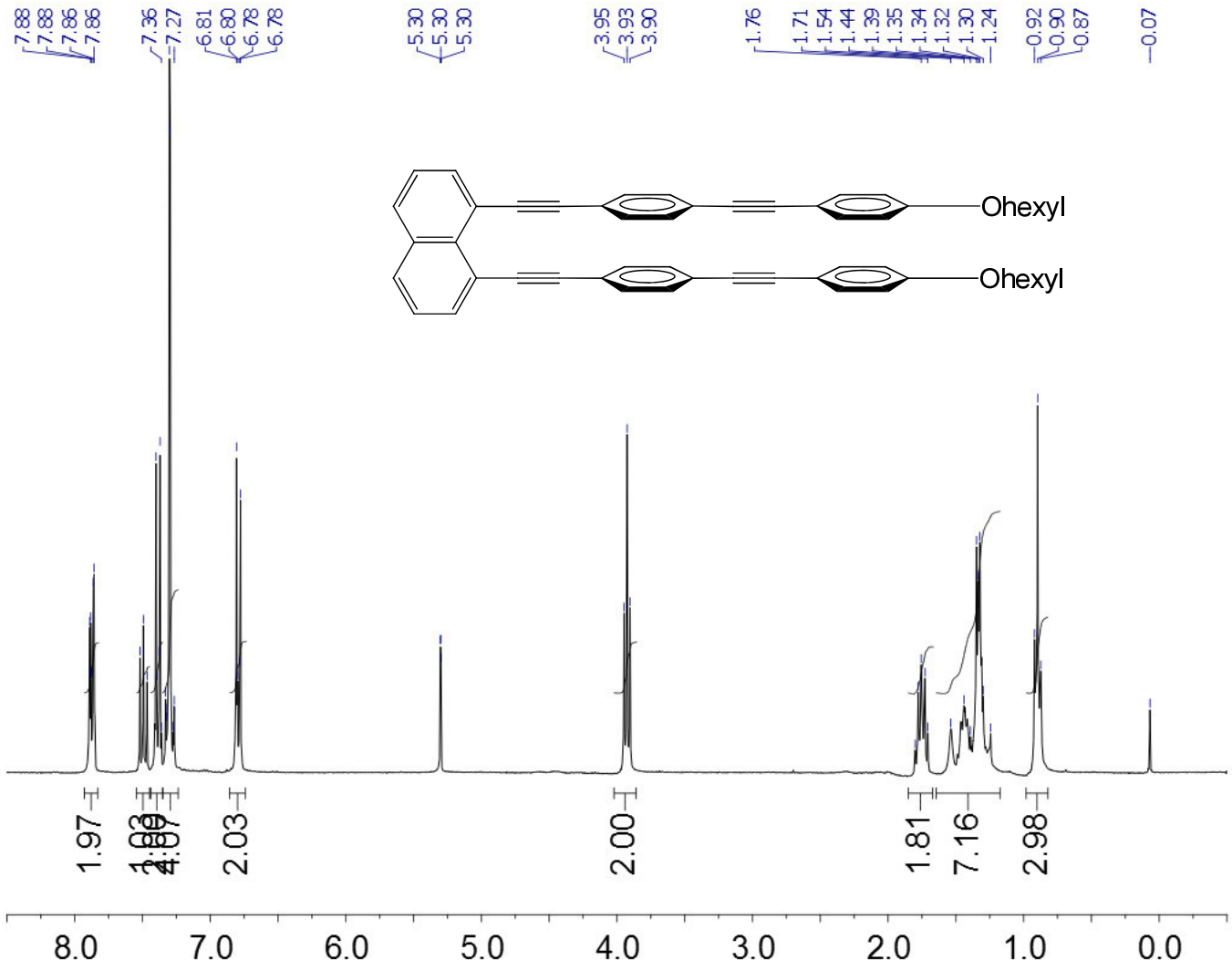

Figure B72. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1,8-(4-(4-Hexyloxyphenylethynyl)phenyl)ethynyl)naphthalene, IV-10**.

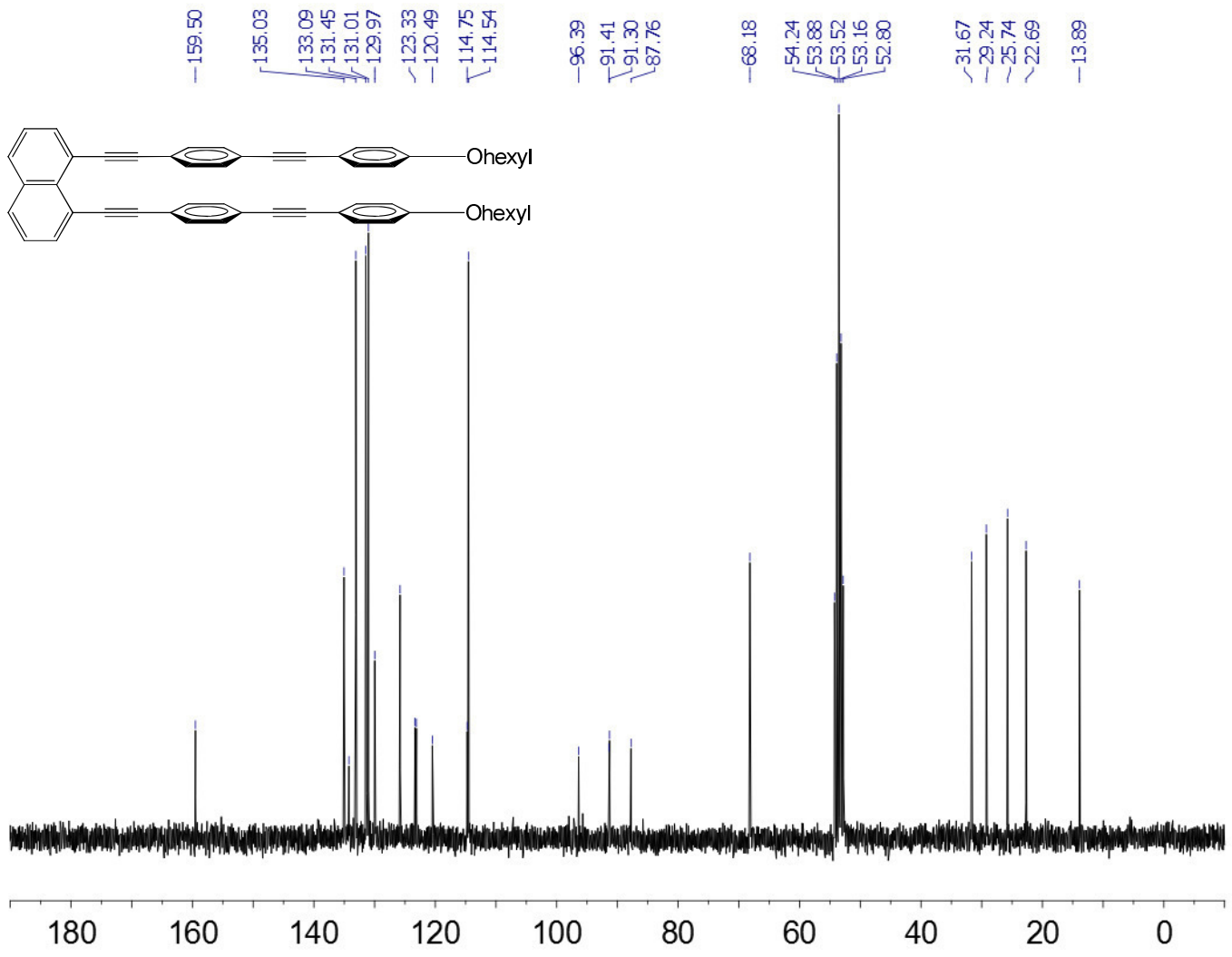

Figure B73. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1,8-(4-(4-Hexyloxyphenylethynyl)phenyl)ethynyl)naphthalene, IV-10**.

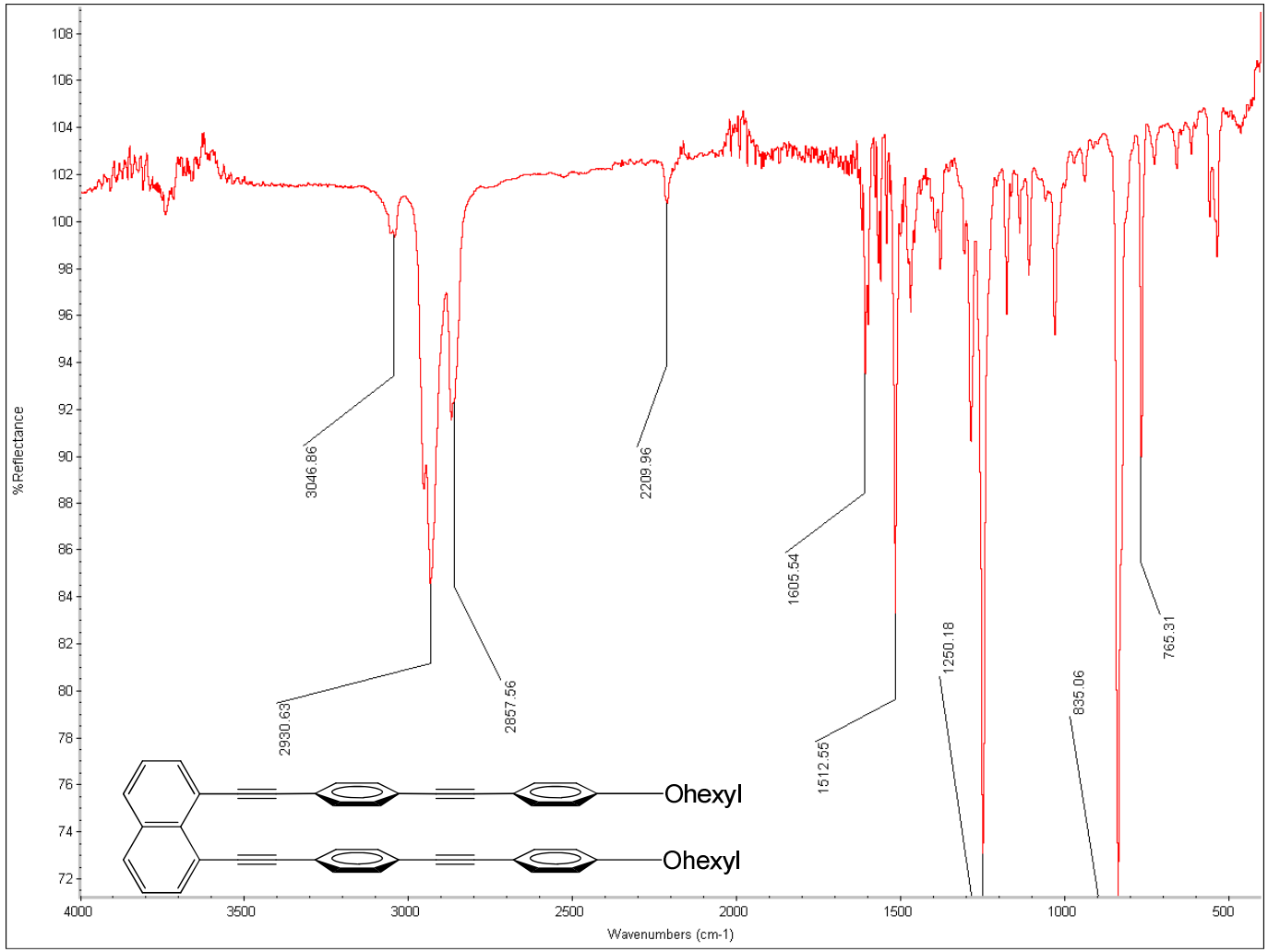

Figure B74. IR (ATIR, neat) of **1,8-(4-(4-Hexyloxyphenylethynyl)phenyl)ethynyl)naphthalene, IV-10**.

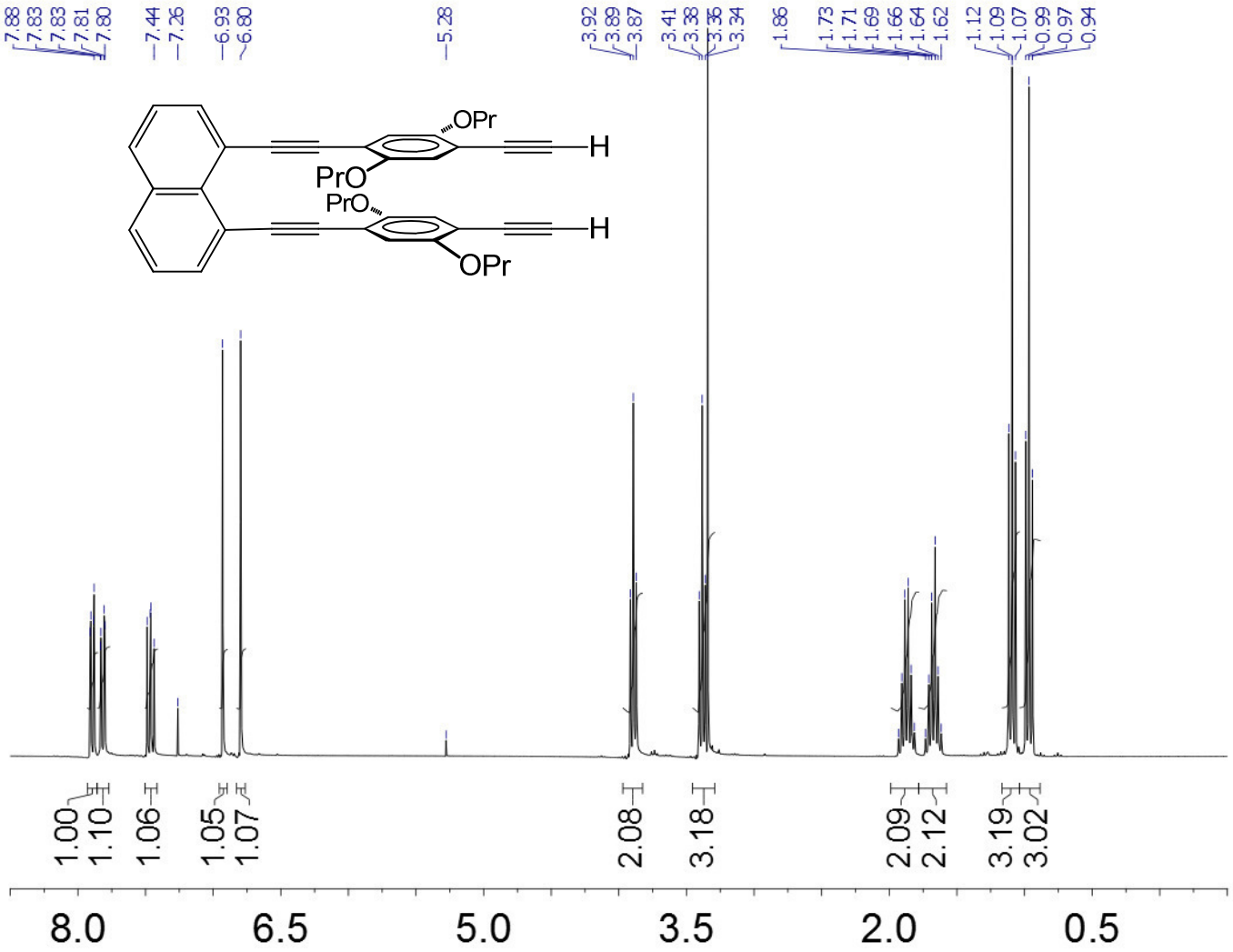

Figure B75. ^{1}HNMR ($CDCl_3$, 300 MHz) of **1,8-(4-Ethynyl-2,5-dipropyloxyphenylethynyl)naphthalene, V-1**.

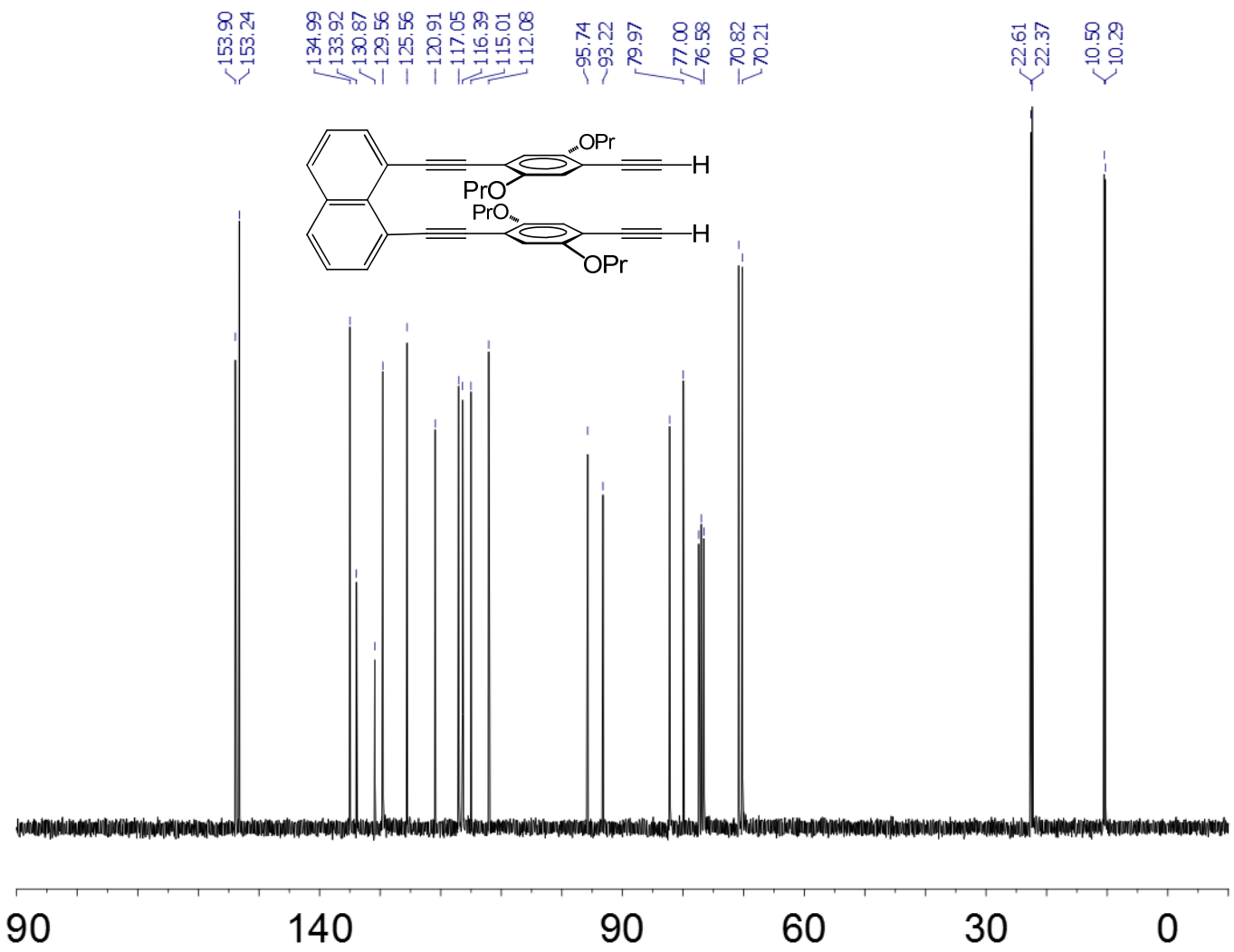

Figure B76. ^{13}CNMR ($CDCl_3$, 300 MHz) of **1,8-(4-Ethynyl-2,5-dipropyloxyphenylethynyl)naphthalene, V-1**.

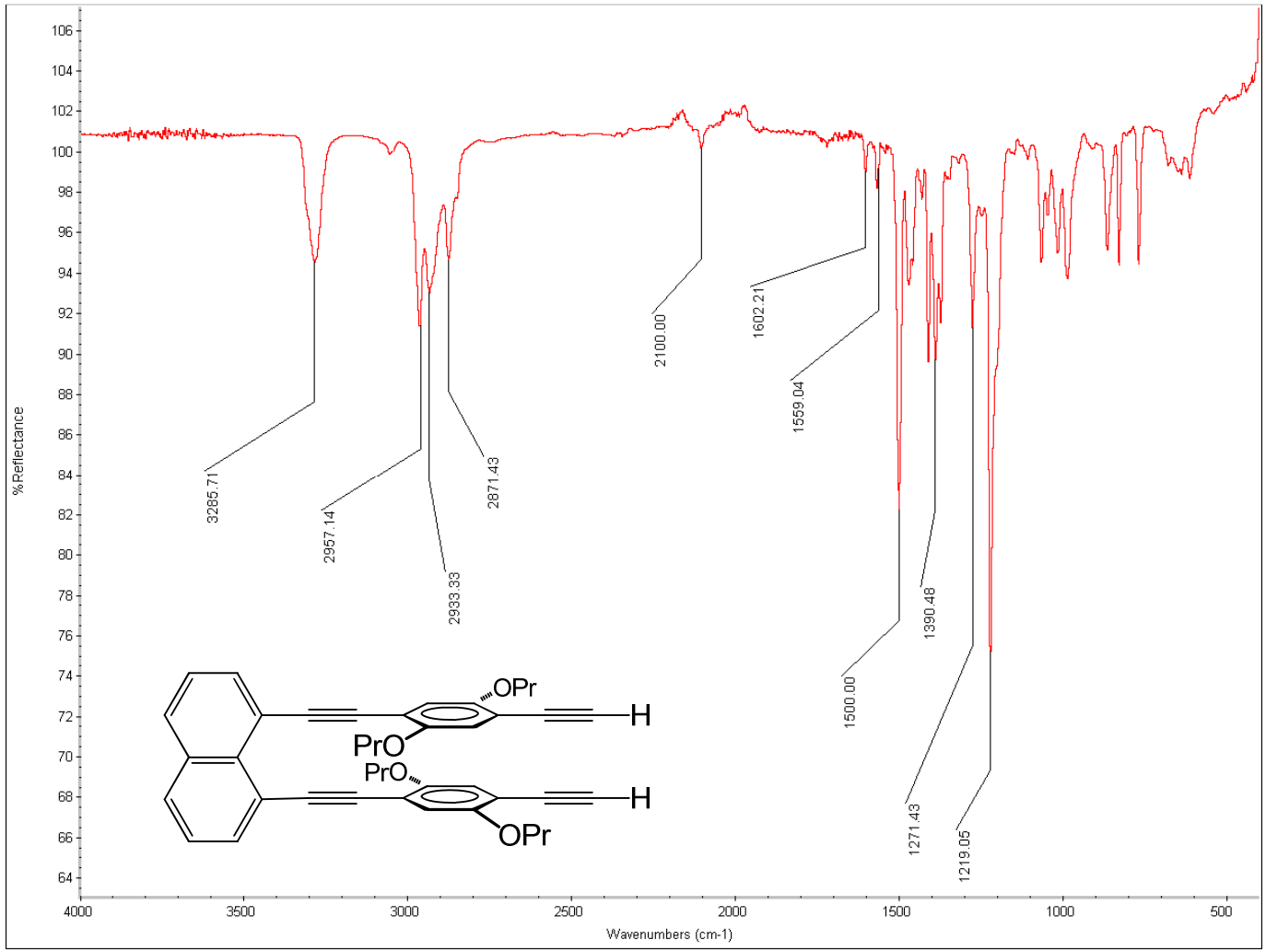

Figure B77. IR (ATIR, neat) of **1,8-(4-Ethynyl-2,5-dipropyloxyphenylethynyl)naphthalene, V-1**.

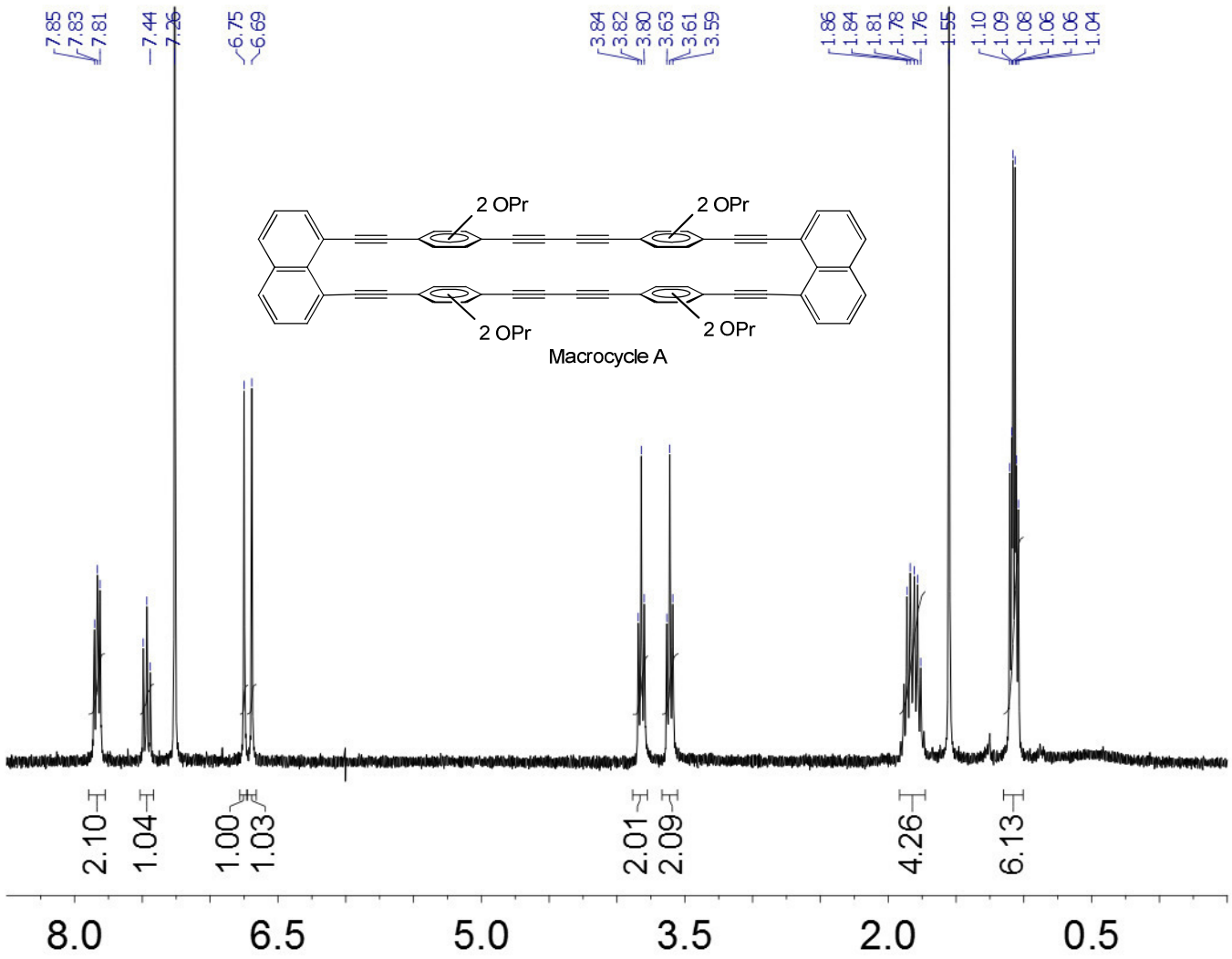

Figure B78. ^{1}HNMR ($CDCl_3$, 300 MHz) of **Di-1,8-(4-ethynyl-2,5-dipropyloxyphenylethynyl)naphthalene), V-2a**.

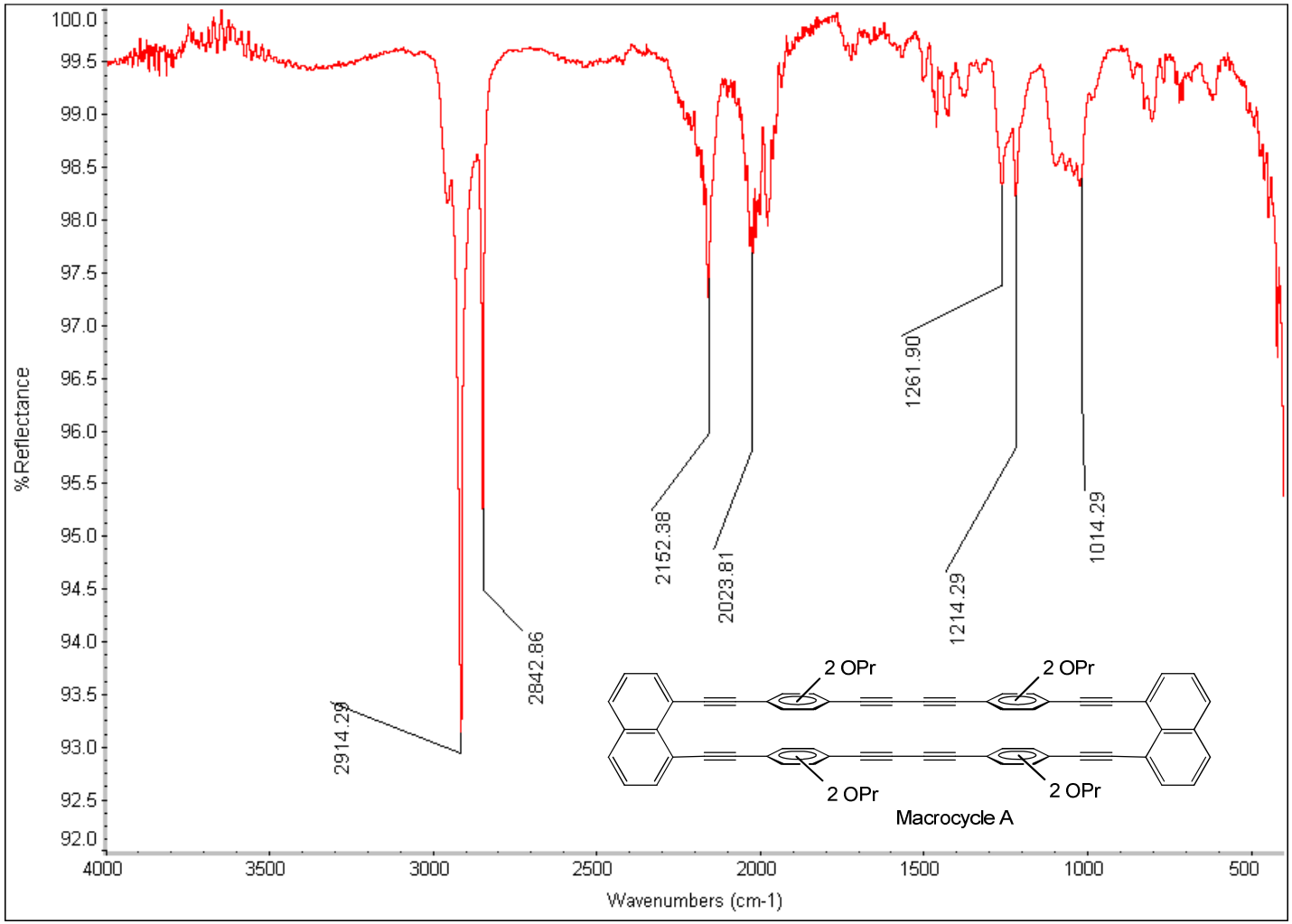

Figure B79. IR (ATIR, neat) of **Di-1,8-(4-ethynyl-2,5-dipropyloxyphenylethynyl)naphthalene), V-2a**.

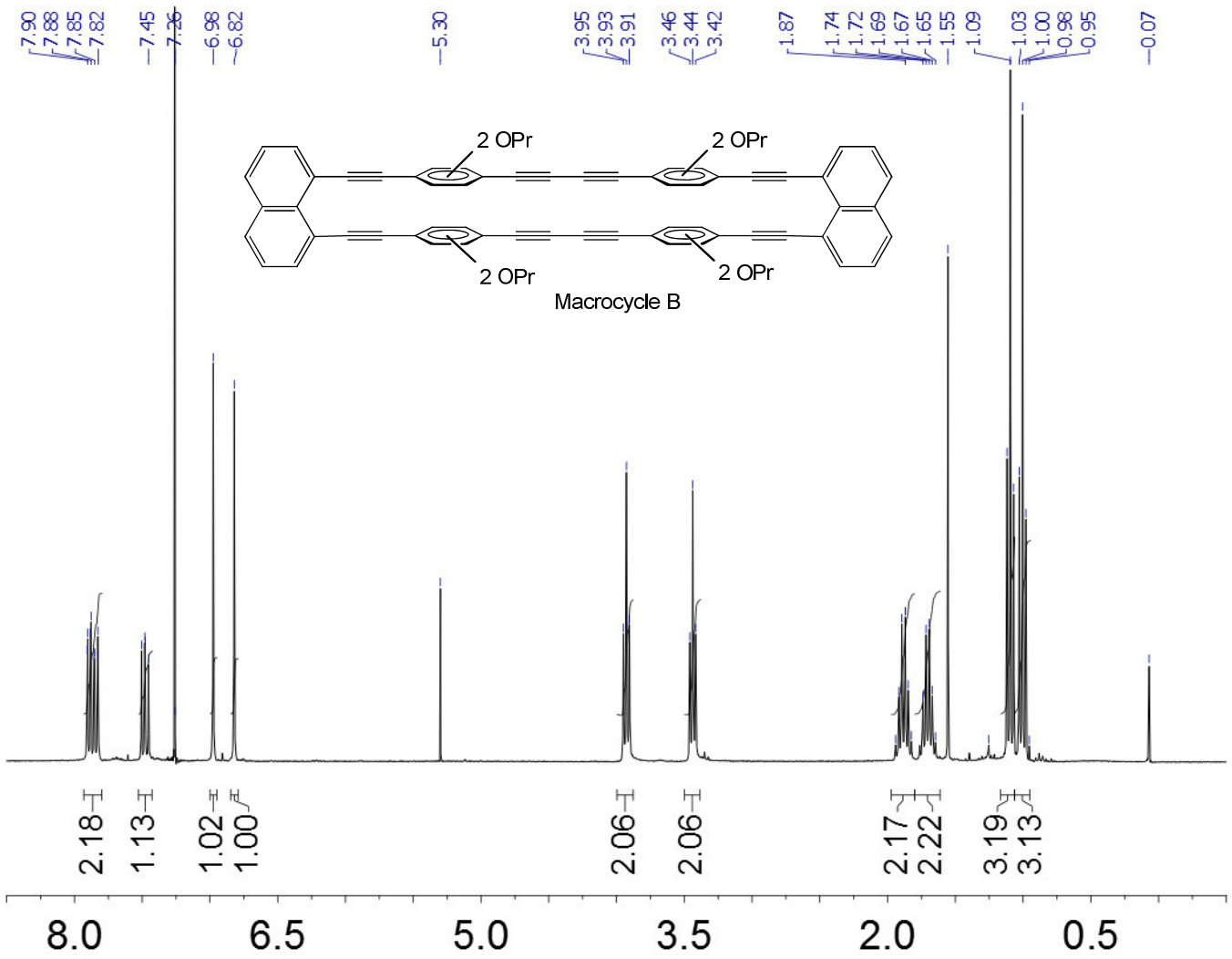

Figure B80. ^{1}HNMR ($CDCl_3$, 300 MHz) of **Di-1,8-(4-ethynyl-2,5-dipropyloxyphenylethynyl)naphthalene), V-2b**.

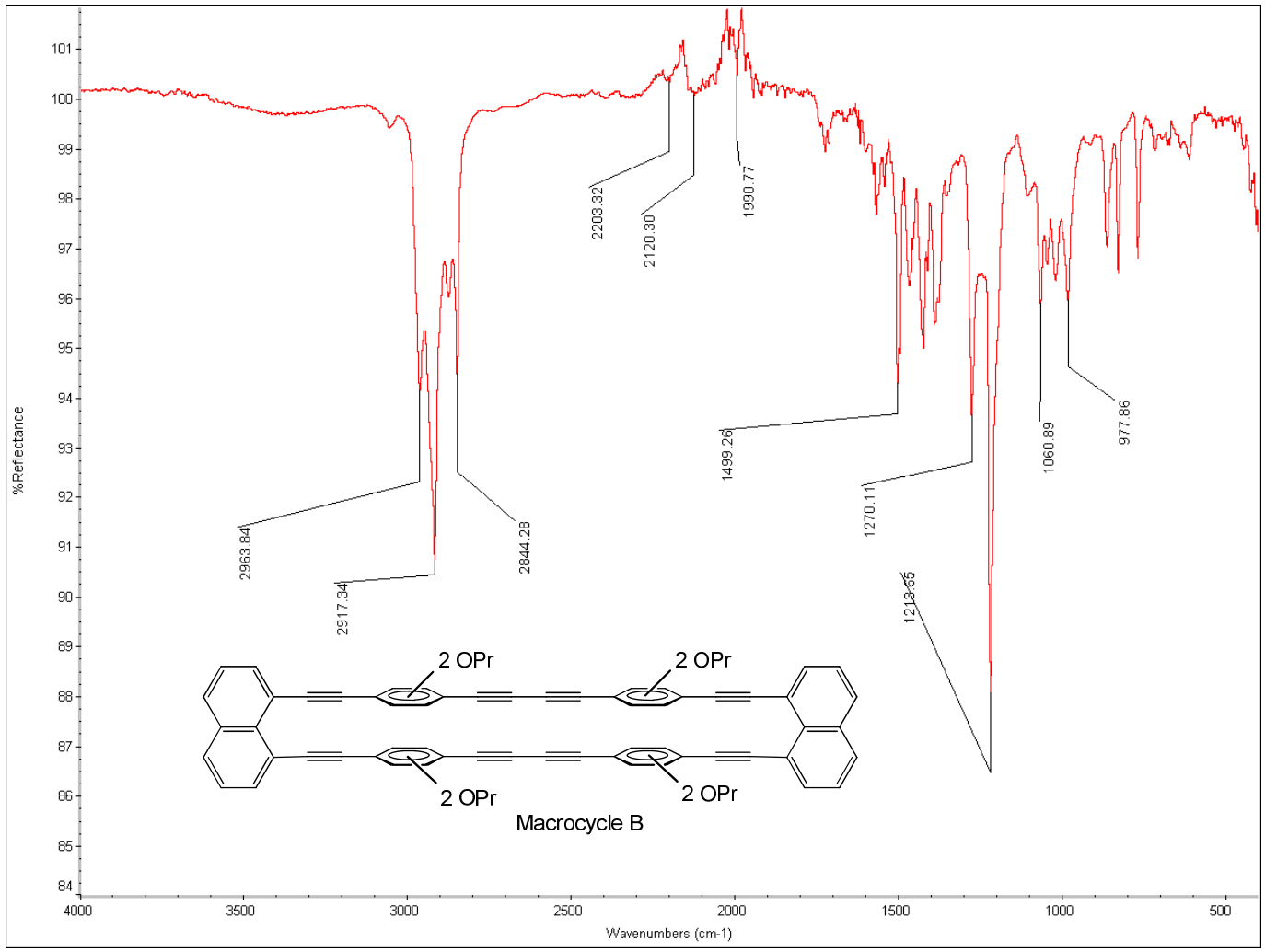

Figure B81. IR (ATIR, neat) of **Di-1,8-(4-ethynyl-2,5-dipropyloxyphenylethynyl)naphthalene), V-2b**.

VITA

Bradley E. Carson

Bradley Carson was born in Durham, North Carolina to parents Johnny and Shirley Carson. He earned his high school diploma from Chapel Hill High School and attended college at Appalachian State University where he earned an A. C. S. Certified B.S. in Chemistry. Over two summers, he participated in undergraduate research under the direction of Dr. Sergei Sheiko at the University of North Carolina at Chapel Hill in 2002 and with Dr. Chris Gorman at North Carolina State University in 2003 as an NSF REU fellow. In 2004, he began graduate studies at The Georgia Institute of Technology under the direction of graduate advisor Dr. David M. Collard where he developed π-stacked phenylene ethynylene oligomers with 1,8-substituted naphthalene bridging scaffolds as models for charge carriers in conjugated polymers. He gave his thesis defense on April 2, 2010. In his spare time, he enjoys watching football and basketball and enjoying the great outdoors.